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THE IDEALLY POLARIZABLE INTERFACE: A SOLVABLE MODEL AND GENERAL SUM RULES

by

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A general thermodynamic argument shows that these sum rules remain valid in three dimensions and for any value of the coupling paramater.

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ABSTRACT

A model for an ideally polarizable interface is proposed where the two sides of the interface are described by two interacting classical one component plasmas of different neutralizing background densities separated by an impermeable membrane. The statistical mechanics of this system is solved exactly in two dimensions at the reduced temperature 2.

The one and two body distribution functions, the potential drop, the differential capacity and the interfacial tension are computed. The main feature of this model is that the potential drop and not the surface charge appears as the natural external variable. Several sum rules are discussed, such as the screening theorems for multipoles, the contact theorem, and Lippmann's equation.

A general thermodynamic argument shows that these sum rules remain valid in three dimensions and for any value of the coupling parameter.

I INTRODUCTION

In recent years there has been much interest in the statistical mechanics
of inhomogeneous charged systems such as the metal electrolyte interface.
Since the real interface is a very complex system,most of the effort
has been directed to understanding models in which the metal side is
an ideally smooth,hard,charged surface,with or without metal boundary
conditions (image forces).Accordingly , the interface is not treated as
an wholy integrated system,in which the metal and the electrolyte are
both treated at the microscopic level,and this is surely a serious
shortcoming of these models.[1]

For instance,if one considers the interface between a liquid metal
(Hg or Ga) and an aqueous electrolyte solution (e.g. KCl),it appears
that the main contribution to the interfacial tension is coming from
the interaction between the metal particles.Since,from Lippmann's
equation, the differential capacity of the interface is the second derivative
of this surface tension with respect to the applied potential,it is
very likely that a sizeable part of this capacity is also due to the
response of the metal.

Indeed this effect has been estimated recently by a model in which
the metal is a quantum mechanical jellium [2,3],and more recently
a jellium interface with an ion-dipole mixture has been considered[4,5].
However, this last model,albeit realistic,is very difficult to handle and
we are far from an accurate numerical solution of the statistical mechanics
of this model.We must remark that even computer simulations cannot be
performed for such a complex case because of the quantum nature of
the metal,and because the discrete solvent of the ionic solution
will require a number of particles that is too large even for modern
computers.

It seems therefore interesting to study simpler models that may
not be as realistic , but still treat the whole interface
at the microscopic level ,and are more tractable mathematically.In particular
we would like to mimic two different situations that occur in electrochemistry

a) the non polarizable interface,in which the potential drop across
the interface is given by Nernst´s equation.The classical example
of this case is the calomel electrode and its behaviour is explained by
the continuous exchange of charged particles between the two sides of
the interface.

b) the polarizable interface,in which the potential
drop does depend on the charge distribution at the interface.

The classical example of this case is the mercury-FNa(aq) interface.
For low values of the potential drop across the interface
a change in the externally applied potential will not simply produce
an increase in the ohmic current intensity,but it will polarize the
surface,producing an excess surface charge on the metal and in the solution.
Above a certain value of the potential however chemical reactions occur and
electrons flow across the interface: At this point the polarizable electrode
becomes unpolarizable ,and behaves much like case (a).

In the present work we consider a 2-dimensional model in which the
two sides of the interface are represented by classical,one component plasmas
(OCP) with different background densities.Of course this is not a realistic
representation of the metal electrolyte interface,but this model has the
feature of being exactly,analytically solvable :Jancovici and coworkers[6,7,8]
have shown that at the special value of the plasma coupling parameter
(or reduced temperature) Γ =2,the partition function and all

the correlation functions of the 2-dimensional OCP can be obtained exactly

On the other hand, as we shall see below, this model reproduces some of the main features of real interfaces and may be useful in providing insight about exact relations such as sum rules and the subtle screening behaviour of Coulomb systems[9].

Recently a solution was found for such a model of the interface where the charged particles (ions) are free to move everywhere [10,11]. In this case the potential drop across the interface depends only on the difference in the chemical potentials of the bulk phases, and any surface charge distribution is perfectly screened by the mobile ions, giving no contribution to the potential drop. Clearly, this model mimics the behaviour of the non polarizable electrode.

In the present paper we present a generalization of this model which mimics the behaviour of the polarizable interface. For that purpose we introduce an impermeable membrane between the two media, which prevents the ions from moving across the interface, while allowing the electrostatic interactions among all ions and background charge. Indeed a completely impermeable membrane is unlikely to exist in nature, and there is always some small but finite current which leaks across the interface. In a limited range of applied potential, however, a system like Hg-FNa(aq.), can be considered as ideally polarizable, because the leakage current is extremely small.

We must point out that in real systems, the concept of an ideally polarizable electrode does not imply the existence of a zero width , mathematical surface ,but there could be a region of limited extent where all particles could coexist [12].

We shall not consider this case here because it is more complex than the former one.

In section 2 we describe the model and the method of solution. Section 3 is devoted to the discussion of 1 and 2 particle density functions,and related sum rules.In Section 4 we compute the total potential drop across the interface, and show that in our model this is indeed the natural external variable,while the surface charge is calculated by means of a closed formula from it.In this sense our model differs from most of the literature, where the charge is the externally fixed variable and the potential drop is calculated from it.The thermodynamics of the system is discussed in Section 5 and pertinent sum rules are given:in particular Lippmann's equation and the contact theorem for this case are deduced.The last section is devoted to a brief discussion of the results.

A short communication of these results has been presented elsewhere[13].

II- <u>MODEL AND METHOD OF SOLUTION</u>

Following the method of Jancovici [8] we start with a system of circular symmetry.In our case it consists of two concentric circles of radii R_1 and R_2 .

The inner region ($0 < r < R_1$) has background charge density $-e\alpha_1/\pi$,where e is the elementary charge,and contains N_1 particules of charge e . This circle is also the impermeable surface that prevents the charged particles from changing sides.

We want to allow for an excess charge density $-e\sigma/\pi$ along the wall then we must have

$$N_1 = \alpha_1 R_1^2 - 2\sigma R_1 \qquad (2.1)$$

The outer region ($R_1 < r < R_2$) has background density $-e\alpha_2/\pi$, excess charge density $e\sigma/\pi$ and contains N_2 particles of charge e. Hence

$$N_2 = \alpha_2 (R_2^2 - R_1^2) + 2\sigma R_2 \qquad (2.2)$$

the system is thus globally neutral. The thermodynamic limit is obtained letting the number of particles and the radii go to infinity with α_1, α_2 and σ constant.

The plasma coupling parameter is $\Gamma = \beta e^2 = 2$ where $\beta = 1/kT$ is the thermal Boltzmann factor and T is the temperature.

The Coulomb potential between two particles at a distance r is

$$v(r) = -e^2 \ln\left(\frac{r}{L}\right) \qquad \text{where L is some scaling length.}$$

The first step is to compute the total potential energy of the system. We find

$$V = V_0 + \frac{1}{2}e^2 \left\{ -\sum_{i>j}^{N} \ln |\vec{r}_i - \vec{r}_j|^2 + \alpha_1 \sum_{i=1}^{N_1} (r_i^2 - R_1^2) + \alpha_2 \sum_{i=N_1+1}^{N} (r_i^2 - R_1^2) \right.$$

$$\left. + (\alpha_1 - \alpha_2) R_1^2 \sum_{i=N_1+1}^{N} \ln \left(\frac{r_i}{R_1}\right)^2 \right\} \qquad (2.3)$$

where $\vec{r}_i$ is the position of ion i, $N = N_1 + N_2$ and V_0 is a constant background term

$$V_0 = \frac{e^2}{2} \left\{ (\alpha_1 - \alpha_2) R_1^2 \left[(\alpha_1 - \alpha_2) R_1^2 + 2\alpha_2 R_2^2 \right] \ln R_1 + \alpha_2^2 R_2^4 \ln R_2 + \frac{1}{4}\alpha_1 R_1^4 \right.$$

$$\left. + \alpha_2^2 (R_1^2 R_2^2 - R_1^4/4 - 3R_2^4/4) \right\} \qquad (2.4)$$

Note that the excess charge density $e\sigma$ does not appear explicitly in (2.3) and (2.4).

In computing the canonical partition function, the angular integrations can be readily performed expanding a Vandermonde determinant [7,8] and we get

$$Z_N = \frac{1}{N_1! N_2!} \int d\vec{r}^N \, e^{-\beta V}$$

$$= e^{-\beta V_0} \frac{(2\pi)^N}{N_1! N_2!} \int_0^{R_1} dr^{N_1} e^{-\alpha_1 \sum_{i=1}^{N_1}(r_i^2 - R_1^2)} \int_{R_1}^{R_2} dr^{N_2} e^{-\alpha_2 \sum_{i=N_1+1}^{N}(r_i^2 - R_1^2)} \prod_{i=N_1+1}^{N} \left(\frac{r_i}{R_1}\right)^{2(\alpha_2 - \alpha_1)R_1^2}$$

$$\cdot \sum_{\mathcal{P}} \mathcal{P} \left[r_1^0 r_2^2 r_3^4 \cdots r_N^{2(N-1)} \right] \qquad (2.5)$$

where $\mathcal{P}$ is the permutation operator of all N particles.

This can be written

$$Z_N = e^{-\beta V_0}(2\pi)^N \sum_{\mathcal{P}'} \mathcal{P}' \left[\prod_{n=0}^{N_1-1} \int_0^{R_1} dr\, r^{2n+1} e^{-\alpha_1(r^2-R_1^2)} \prod_{n=N_1}^{N-1} \int_{R_1}^{R_2} dr\, \frac{r^{2n_2+1}}{R_1^{2(n_2-n)}} e^{-\alpha(r^2-R_1^2)} \right.$$

where $n_2 = n + (\alpha_2 - \alpha_1)R_1^2$

$$(2.6)$$

and $\mathcal{P}'$ is the permutation operator that exchanges the labels $\{0, N_1-1\}$ with labels $\{N_1, N-1\}$ in all possible ways.

Introducing the functions

$$\phi^1(n) = \frac{e^{\alpha_1 R_1^2}}{\alpha_1^{n+1}} \gamma(n+1, \alpha_1 R_1^2)$$

and

$$(2.7)$$

$$\phi^2(n) = \frac{e^{\alpha_2 R_1^2}}{\alpha_2^{n_2+1} R_1^{2(n_2-n)}} \left[\gamma(n_2+1, \alpha_2 R_2^2) - \gamma(n_2+1, \alpha_2 R_1^2) \right]$$

where

$$\gamma(n+1, R_1^2) = \int_0^{R_1^2} e^{-u} u^n\, du$$

is the incomplete gamma function, we get

$$Z_N = e^{-\beta V_0} \pi^N \sum_{\mathcal{P}'} \mathcal{P}' \left[\phi^1(0)\, \phi^1(1) \dots \phi^1(N_1-1)\, \phi^2(N_1) \dots \phi^2(N-1) \right]$$

$$(2.8$$

This can be written in a more convenient form factorizing the term

$$\prod_{n=0}^{N_1-1} \phi^1(n) \prod_{n=N_1}^{N-1} \phi^2(n) .$$

We find

$$Z_N = Z_N^0 \,\Xi \qquad (2.9)$$

where

$$Z_N^0 = e^{-\beta V_0} \pi^N \prod_{n=0}^{N_1-1} \phi^1(n) \prod_{n=N_1}^{N-1} \phi^2(n) \qquad (2.10)$$

and Ξ is the generating function

$$\boxed{\Xi} = 1 + \sum_{n_1=1}^{N_1} \sum_{m_1=N_1+1}^{N} \frac{\chi(m_1)}{\chi(m_1)} + \sum_{n_1=1,\,n_2=n_1}^{N_1-1} \sum_{m_1=N_1+1,\,m_2=m_1}^{N-1} \frac{\chi(m_1)\,\chi(n_2+1)}{\chi(m_1)\,\chi(m_2+1)}$$

$$+ \sum_{n_1=1,\,n_2=n_1,\,n_3=n_2}^{N_1-2} \sum_{m_1=N_1+1,\,m_2=m_1,\,m_3=m_2}^{N-2} \frac{\chi(n_1)\,\chi(n_2+1)\,\chi(n_3+2)}{\chi(m_1)\,\chi(m_2+1)\,\chi(m_2+2)} + \dots$$

where   (2.11)

$$\chi(n+1) = \phi^2(n)/\phi^1(n)$$

In (2.11) it appears that in the limit R_2, $R_1 \to \infty$, the dominant values of the arguments of the summations are those with indices close to N_1. The incomplete gamma function can be expanded in this limit using the asymptotic formula [6]

$$\gamma(n+1, \alpha_1 R_1^2) = \frac{1}{2}\sqrt{2n}\; e^{-n} n^n \left[\operatorname{erfc}(-t) + O\!\left(\frac{1}{R_1}\right) \right] \qquad (2.12)$$

where

$$t = \frac{\alpha_1 R_1^2 - n}{\sqrt{2n}}$$

and

$$\operatorname{erfc}(t) = \frac{2}{\sqrt{\pi}} \int_t^\infty e^{-u^2}\, du$$

is the complementary error function.

This yields, after some manipulations

$$\chi(n) = \chi(t) + O\!\left(\frac{1}{R_1}\right)$$

where

$$\chi(t) = m\; e^{(m^2-1)t^2}\; \frac{\operatorname{erfc}(mt)}{\operatorname{erfc}(-t)} \qquad (2.13)$$

and $m = \sqrt{\dfrac{\alpha_1}{\alpha_2}}$

The deviations of $\boxed{\Xi}$ from unity are due to "surface" contributions. In a first approximation, we can simply neglect these contributions. This will be a mean field approximation (MFA). The neglect of the variation of the indices in the computation of $\boxed{\Xi}$ constitutes a second approximation which will be found to be surprisingly accurate.

a) The mean field approximation (MFA)

Since $\Box = 1$ we have

$$\mathcal{Z}_N = \mathcal{Z}_N^{\circ} = e^{-\beta V_o} \pi^N \widetilde{\prod_{n=o}^{N_1-1}} \phi^1(n) \widetilde{\prod_{n=N_1}^{N-1}} \phi^2(n) \qquad (2.14)$$

This approximation has a physical meaning: It is clear that

that $\mathcal{Z}_N^{\circ}$ is the partition function of the uncoupled system where one

neglects the correlations of the charge fluctuations between the two

sides of the interface. In this sense it is a bona fide mean field

approximation. The system is the superposition of two subsystems: The inner

OCP enclosed by a ring of radius R_1 with charge density $e\sigma/\pi$

and the outer OCP enclosing the charged ring of radius R_1 and charge

density $-e\sigma/\pi$.

These cases have been already solved in the literature[8,14], so

that we merely quote the results for the partition function and the

one body density. For the inner circle subsystem

$$\mathcal{Z}_{N_1} = \frac{1}{N_1!} \int d\vec{r}^{N_1} e^{-\beta V_1} = e^{-\beta V_1^{\circ}} \pi^{N_1} \widetilde{\prod_{n=o}^{N_1-1}} \phi^1(n) \qquad (2.15)$$

where V_1° is the constant background term

$$V_1^{\circ} = \frac{e^2}{2} \left[N_1^2 \ln R_1 + \frac{1}{4} \alpha_1^2 R_1^4 \right] \qquad (2.16)$$

and for the outer ring subsystem

$$\mathcal{Z}_{N_2} = \frac{1}{N_2!} \int d\vec{r}^{N_2} e^{-\beta V_2} = \frac{e^{-\beta V_2^{\circ}}}{R_1^{2N_1 N_2}} \pi^{N_2} \widetilde{\prod_{n=N_1}^{N-1}} \phi^2(n) \qquad (2.17)$$

where

$$V_2^{\circ} = \frac{e^2}{2} \left\{ \left(N_2^2 - \alpha_2^2 R_2^4 \right) \ln R_1 + \alpha_2^2 R_2^4 \ln R_2 + \alpha_2^2 \left(R_1^2 R_2^2 - R_1^4/4 - 3R_2^4/4 \right) \right\} \qquad (2.18)$$

and the particles have been relabelled from $\{0, N_2-1\}$ to $\{N_2, N-1\}$.

It can be easily verified that

$$e^{-\beta V_o} = \frac{e^{-\beta(V_1^{\circ} + V_2^{\circ})}}{R_1^{2N_1 N_2}} \qquad (2.19)$$

hence

$$Z_N^\bullet = Z_{N_1} Z_{N_2} \qquad (2.20)$$

In the limit of a "planar" interface $(R_2, R_1 \to \infty)$, the corresponding one
particle density profile is [8,14]

$$\rho^0(x) = \begin{cases} \dfrac{2\alpha_1}{\pi^{1/2}} \displaystyle\int_{-\sigma\sqrt{2\alpha_1}}^{\infty} \dfrac{\exp\left[-(t+x\sqrt{2\alpha_1})^2\right]}{\mathrm{erfc}(-t)}\, dt & x < 0 \\[4mm] \dfrac{2\alpha_2}{\pi^{1/2}} \displaystyle\int_{-\sigma\sqrt{2\alpha_2}}^{\infty} \dfrac{\exp\left[-(t-x\sqrt{2\alpha_2})^2\right]}{\mathrm{erfc}(-t)}\, dt & x > 0 \end{cases} \qquad (2.21)$$

with origin of coordinates at the wall $(x = r - R_1)$.

In two dimensions $\Gamma = 2$ corresponds a somewhat weak coupling
for the bulk ions, so we can expext that this mean field approximation
will yield sensible results for not too large surface charges.

We think that for any realistic model of the interface this will be
a first approximation. If we also neglect the contributions of the "metal" side
(say, the RHS of the interface), then we will recover a model of the interface
similar to the one discussed in most of the literature (the "primitive" electrode

b) Second approximation.

A better, perhaps not as transparent physically, approximation
can be obtained by neglecting end terms in the summations (2.11).

Using the identity

$$\sum_{i=1}^{N}\sum_{j=i}^{N} = \sum_{j=1}^{N}\sum_{i=1}^{j}$$

$\sqsupset\atop\sqsubset$ can be written

$$\sqsupset\atop\sqsubset = 1 + \sum_{n_1=1}^{N_1}\sum_{m_1=N_1+1}^{N} \frac{X(n_1)}{X(m_1)} + \sum_{n_1=2,\,n_2=1}^{N_1,\,n_1-1}\sum_{m_1=N_1+1,\,m_2=m_1+1}^{N-1,\,N} \frac{X(n_1)\,X(n_2)}{X(m_1)\,X(m_2)}$$

$$+ \sum_{n_1=3,\,n_2=2,\,n_3=1}^{N_1,\,n_1-1,\,n_2-1}\sum_{m_1=N_1+1,\,m_2=m_1+1,\,m_3=m_2+1}^{N-2,\,N-1,\,N} \frac{X(n_1)\,X(n_2)\,X(n_3)}{X(m_1)\,X(m_2)\,X(m_3)} + \dots \qquad (2.22)$$

which shows that the terms neglected by extending the sums at the ends
of the intervals are small (see (2.13)). Then we write

$$\Xi = 1 + \sum_{n_1=1}^{N_1} \sum_{m_1=N_1+1}^{N} \frac{\chi(n_1)}{\chi(m_1)} + \sum_{n_1=1, n_2=1}^{N_1,\ n_2-1} \sum_{m_1=N_1+1, m_2=m_1+1}^{N} \frac{\chi(n_1)\,\chi(n_2)}{\chi(m_1)\,\chi(m_2)}$$

$$+ \sum_{n_1=1, n_2=1, n_3=1}^{N_1,\ n_1-1,\ n_2-1} \sum_{m_1=N_1+1, m_2=m_1+1, m_3=m_2+1}^{N} \frac{\chi(n_1)\,\chi(n_2)\,\chi(n_3)}{\chi(m_1)\,\chi(m_2)\,\chi(m_3)} + \dots \qquad (2.23)$$

In the limit $N_1 \to \infty$, the sums can be replaced by integrals over the new variable $t = \dfrac{\sqrt{}\,R_1^2 - n}{\sqrt{2n}}$ and using the formula

$$\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \dots \int_0^{\tau_{N-1}} d\tau_N\ f(\tau_1) f(\tau_2) f(\tau_3) \dots f(\tau_N) = \frac{1}{N!} \left[\int_0^t f(\tau)\, d\tau \right]^N$$

we get

$$\Xi \sim 1 + \frac{2N_1\, K_1 K_2}{(1!)^2} + \frac{(2N_1\, K_1 K_2)^2}{(2!)^2} + \dots \qquad (2.24)$$

where

$$K_1 = \int_{-\infty}^{\sqrt{2/a_1}} \frac{dt}{\chi(t)} \qquad \text{and} \qquad K_2 = \int_{r\sqrt{2/a_1}}^{\infty} \chi(t)\, dt \qquad (2.25)$$

which can be recognized as the expansion of the modified Bessel function $I_0 \left(2\sqrt{N_1}\,\sqrt{2K_1 K_2} \right)$ [15].

Asymptotically

$$\Xi \sim \frac{e^{2\sqrt{2N_1}\,\sqrt{K_1 K_2}}}{\left(4\pi\sqrt{2N_1}\,\sqrt{K_1 K_2} \right)^{1/2}} \qquad (2.26)$$

so that

$$\lim_{N_1 \to \infty} \frac{1}{\sqrt{N_1}} \ln \Xi = 2\sqrt{2K_1 K_2} \qquad (2.27)$$

We shall discuss this interesting approximation below.

c) Exact solution.

Instead of using (2.11) to compute Z_N the exact partition function of the coupled system, we could represent it in a much more compact form using a device similar to a grand canonical ensemble calculation. Consider

now that all particles are indistinguishable and can move freely
throughout the entire system, but assume that the particles of the inner
region have a fugacity z different from that of the outer region, which
we take as the reference and set it to the value of 1.

It is straightforward to see that the partition function Z_N is the
coefficient of z^{N_i} in the polynomial

$$Z(z) = e^{-\beta V_0} \pi^N \prod_{n=0}^{N-1} [z \phi^1(n) + \phi^2(n)] \qquad (2.28)$$

which can also be written

$$Z(z) = Z_{N_1} Z_{N_2} \prod_{n=1}^{N_1} [z + \chi(n)] \prod_{n=N_1+1}^{N} [z/\chi(n) + 1] \qquad (2.29)$$

Using the theorem of residues, we finally get

$$\Xi = \frac{1}{2i\pi} \oint \frac{dz}{z} \prod_{n=1}^{N_1} [\chi(n) z^{-1} + 1] \prod_{n=N_1+1}^{N} [\chi(n)^{-1} z + 1] \qquad (2.30)$$

which can be evaluated asymptotically by the method of steepest descents.
The path of integration is a circle centered at the origin.

Define

$$Y(z) = \sum_{n=1}^{N_1} \ln [\chi(n) z^{-1} + 1] + \sum_{n_i=N_1+1}^{N} \ln [\chi(n)^{-1} z + 1] \qquad (2.31)$$

then

$$\Xi = \frac{1}{2i\pi} \oint e^{Y(z)} \frac{dz}{z} \qquad (2.32)$$

The saddle point is located at the positive real z axis. The location
of the saddle point is found by solving the equation

$$\frac{\partial Y(\zeta)}{\partial \zeta} \equiv -\frac{1}{\zeta_0} \sum_{n=1}^{N_1} \frac{\chi(n)}{\chi(n)+\zeta_0} + \sum_{n=N_1+1}^{N} \frac{1}{\chi(n)+\zeta_0} = 0 \tag{2.33}$$

Taking again the limit of an infinitely large system, and changing to

the variable $t = \frac{\alpha_1 R_1^2 - n}{\sqrt{2n}}$

this equation becomes

$$\int_{\sigma\sqrt{2}/\alpha_1}^{\infty} \frac{\chi(t)}{\chi(t)+\zeta_0} dt = \int_{-\sigma\sqrt{2}/\alpha_1}^{\infty} \frac{\zeta_0}{\chi(-t)+\zeta_0} dt \tag{2.34}$$

For $m=1$ we have $\chi(-t) = \chi(t)^{-1}$

so that $\zeta_0(-\sigma) = \zeta_0(\sigma)^{-1}$

and $\zeta_0(\sigma=0) = 1$. In the general case this equation must be solved numerically

for given values of the surface charge density $e\sigma$.

Now we take $\zeta = \zeta_0 \exp(i\theta)$ and then integral (2.32) yields

$$\Xi \sim \frac{e^{Y(\zeta_0)}}{\zeta_0 \sqrt{2\pi Y''(\zeta_0)}} \tag{2.35}$$

where

$$Y(\zeta_0) \sim R_1 \sqrt{2\alpha_1} \left[\int_{-\infty}^{\sigma\sqrt{2}/\alpha_1} \ln \frac{\zeta_0 + \chi(t)}{\chi(t)} dt + \int_{\sigma\sqrt{2}/\alpha_1}^{\infty} \ln \frac{\zeta_0 + \chi(t)}{\zeta_0} dt \right] \tag{2.36}$$

Equations (2.9), (2.35) and (2.36) are the exact answers for the

partition function in the fully coupled case.

As one would expect in the asymptotic limit of a large system, $\ln \Xi$

is proportional to the "surface" of the interface. Hence the Helmholtz

free energy of the coupled system differs only by a surface term Δf^s from the

free energy of the uncoupled system:

$$\Delta f^s = - kT \lim_{R_1 \to \infty} \frac{1}{2\pi R_1} \ln \Xi$$

$$= -\frac{\epsilon^2}{4\pi} \sqrt{2\alpha_1} \left[\int_{-\infty}^{\sigma\sqrt{2}/\alpha_1} \ln \frac{\zeta_0 + \chi(t)}{\chi(t)} dt + \int_{\sigma\sqrt{2}/\alpha_1}^{\infty} \ln \frac{\zeta_0 + \chi(t)}{\zeta_0} dt \right] \tag{2.37}$$

This equation gives the thermodynamic properties of our model:It will be discussed in detail in section 5.

A very good approximation of the exact solution of the saddle point equation (2.34) can be obtained if we assume that

$$\chi(t) \gg \zeta_0 \quad \text{for} \quad t < \sigma \sqrt{2/\alpha_1}$$

$$\chi(t) \ll \zeta_0 \quad \text{for} \quad t > \sigma \sqrt{2/\alpha_1} \tag{2.38}$$

and expand in the small variable $\chi(t)/\zeta_0$ or $\zeta_0/\chi(t)$ in (2.34).We find to first order

$$\zeta_0 = \left(\frac{K_2}{K_1}\right)^{1/2} \tag{2.39}$$

where K_1 and K_2 are defined in (2.25).The same procedure applied to (2.37) yields

$$\Delta f^s = -\frac{e^2}{2\pi} \sqrt{2\alpha_1} \sqrt{K_1 K_2} \tag{2.40}$$

But this is also the result obtained directly from (2.27).Hence this approximation is strictly equivalent to the one of subsection (2-b).

3. DENSITY PROFILE AND PAIR CORRELATION FUNCTIONS

The same methods used in obtaining the partition function can be used in obtaining the one and two body correlation functions.

a) Density profile.

From equation (2.28) we find that the density profile is for $r < R_1$

$$\rho(r) = \frac{1}{\pi Z_N} \sum_{n=0}^{N-1} e^{-\alpha_1 (r^2 - R_1^2)} r^{2n} a_{N_1-1} \tag{3.1}$$

where a_{N_1-1} is the coefficient of ζ^{N_1-1} in the polynomial $\dfrac{Z(\zeta)}{\zeta \varphi'(n) + \varphi^2(n)}$

Hence,after some manipulations,we get

$$\rho(r) = \frac{1}{\pi} \frac{1}{\square} \sum_{n=1}^{N} f_n^1(r) \frac{1}{2i\pi} \oint d\zeta \frac{e^{Y(\zeta)}}{\zeta + \chi(n)} \qquad (3.2)$$

where

$$f_{n+1}^1(r) = \frac{e^{-\alpha_1(r^2 - R_1^2)}}{\phi^1(n)} r^{2n}$$

Similarly, for $r > R_1$

$$\rho(r) = \frac{1}{\pi} \frac{1}{\square} \sum_{n=1}^{N} f_n^2(r) \frac{1}{2i\pi} \oint \frac{d\zeta}{\zeta} \frac{\chi(n)}{\zeta + \chi(n)} e^{Y(\zeta)} \qquad (3.3)$$

where

$$f_{n+1}^2(r) = \frac{e^{-\alpha_2(r^2 - R_1^2)}}{\phi^2(n)} \frac{r^{2n_2}}{R_1^{2(n_2-n)}} \qquad \left(n_2 = n + (\alpha_2 - \alpha_1) R_1^2 \right)$$

In the plane interface limit we use again the asymptotic expansion
of the incomplete gamma function and replace the sums by integrals over
t. The asymptotic behaviour of the contour integrals is again obtained
by steepest descents. The saddle point is located at the same position ζ_0
as before.

After some manipulations we obtain

$$\rho(x) = \begin{cases} \dfrac{2\alpha_1}{\pi^{3/2}} \zeta_0 \displaystyle\int_{-\infty}^{+\infty} \dfrac{\exp\left[-(t + x\sqrt{2\alpha_1})^2 \right]}{\zeta_0\, \mathrm{erfc}(-t) + m\, e^{(m^2-1)t^2} \mathrm{erfc}(mt)}\, dt & x < 0 \\[4mm] & \qquad (3.4) \\[2mm] \dfrac{2\alpha_1}{\pi^{3/2}} \displaystyle\int_{-\infty}^{+\infty} \dfrac{\exp\left[-(mt + x\sqrt{2\alpha_2})^2 \right]}{m\, \mathrm{erfc}(mt) + \zeta_0\, e^{(1-m^2)t^2} \mathrm{erfc}(-t)}\, dt & x > 0 \end{cases}$$

which can be written in a more compact form

$$\rho(x) = \frac{2}{\pi^{3/2}} g(x) \int_{-\infty}^{+\infty} \frac{\exp(-2tx\sqrt{2})}{\dfrac{\zeta_0}{\sqrt{\alpha_1}} \mathrm{erfc}(-t/\sqrt{\alpha_1}) e^{t^2/\alpha_1} + \dfrac{1}{\sqrt{\alpha_2}} \mathrm{erfc}(t/\sqrt{\alpha_2}) e^{t^2/\alpha_2}}\, dt \qquad (3.5)$$

where

$$g(x) = \begin{cases} z_0 \exp(-2\alpha_1 x^2) & , \quad x < 0 \\ \exp(-2\alpha_2 x^2) & , \quad x > 0 \end{cases} \qquad (3.6)$$

Although the physics of the present model is not quite the same as that of the permeable membrane [10,11], it is interesting to note that we recover the density profile of this case when $z_0 = 1$. In this former case the density of mobile ions was always continuous. In the present model, however, there is a discontinuity in the density profile at the interface:

$$\frac{\rho_1(0)}{\rho_2(0)} = z_0 \qquad (3.7)$$

For $m=1$ ($\alpha_1 = \alpha_2 = \alpha$) these contact values can be computed explicitly

$$\rho_1(0) = z_0 \, \rho_2(0) = \frac{\alpha}{\pi} \frac{z_0}{z_0 - 1} \ln z_0 \qquad (3.8)$$

For $m=1$ and $\sigma = 0$ one obtains the expected result

$$\rho(x) = \text{constant}$$

which means that the system behaves as if there would be no wall.

The approximation of subsection (2-b) is of interest because the density profile $\rho(x)$ is the sum of the density of the MFA plus a perturbation. Using (2.38) we find

$$\rho(x) = \rho^0(x) + \Delta\rho(x) \qquad (3.9)$$

where

$$\Delta\rho(x) = \frac{2\alpha_1}{\pi^{1/2}} \begin{cases} \left(\frac{K_2}{K_1}\right)^{1/2} \displaystyle\int_{-\infty}^{\sigma\sqrt{2}/4_1} dt \, \frac{e^{-(t+x\sqrt{2\alpha_1})^2}}{m \, e^{(m^2-1)t^2} \, \text{erfc}(mt)} - \left(\frac{K_1}{K_2}\right)^{1/2} \displaystyle\int_{\sigma\sqrt{2}/4_1}^{\infty} dt \, \frac{e^{(m^2-1)t^2} \, m \, \text{erfc}(mt)}{[\text{erfc}(-t)]^2} e^{-(t+x\sqrt{2\alpha_1})^2} & , \, x < 0 \\[4mm] \left(\frac{K_1}{K_2}\right)^{1/2} \displaystyle\int_{\sigma\sqrt{2}/4_1}^{\infty} dt \, \frac{e^{(m^2-1)t^2}}{\text{erfc}(-t)} e^{-(mt+x\sqrt{2\alpha_2})^2} - \left(\frac{K_2}{K_1}\right)^{2} \displaystyle\int_{-\infty}^{\sigma\sqrt{2}/4_1} dt \, \frac{\text{erfc}(-t)}{m^2 e^{(m^2-1)t^2} [\text{erfc}(mt)]^2} e^{-(mt+x\sqrt{2\alpha_2})^2} & , \, x > 0 \end{cases}$$

where $\rho^0(x)$ is given by (2.21).

The integrals in (3.5) and (3.9) have been computed numerically for the case $\alpha_1 = 1$, $\alpha_2 = 4$ and $\sigma = -1$. The density profiles are shown in figure 1, together with that of the uncoupled system. Indeed, approximation of subsection (2-b) (or 3.9) is very accurate.

The electroneutrality conditions on each side of the interface imply:

$$\int_0^\infty \left[\rho(x) - \frac{\alpha_2}{\pi}\right] dx = -\int_{-\infty}^0 \left[\rho(x) - \frac{\alpha_1}{\pi}\right] dx = \frac{\sigma}{\pi} \qquad (3.10)$$

In Appendix A we show that these relations can be derived from (2.34), the equation for the saddle point. This constitutes an alternative way of calculating ζ_0 from the surface charge density $e\sigma$.

The approximate solution of section (2-b) satisfies this condition exactly.

b) Two body correlations.

To discuss the 2-body correlation functions we need to consider the three cases of both ions on side 1, both ions on side 2 and one ion on each side of the interface. Since the derivations are very similar, we shall give the details for the last case only

It will be convenient to use a complex number representation of the position of the ions (Jancovici [8]) $z=x+iy=r\ exp(i\theta)$. Then similarly to (3.1) we have

$$\rho(\vec{r_1},\vec{r_2}) = \frac{1}{\pi^2 Z_N} \sum_{\ell,m=0}^{N-1} e^{-\alpha_1(r_1^2-R_1^2)-\alpha_2(r_2^2-R_1^2)} \left(z_1^{2\ell} z_2^{2m} - z_1^{\ell} z_2^{m} z_1^{*m} z_2^{*\ell}\right) \left(\frac{r_2}{R_1}\right)^{2(\alpha_2-\alpha_1)R_1^2} b_{N_1-1}$$

$$(3.11)$$

where b_{N_1-1} is the coefficient of ζ^{N_1-1} in the polynomial

$$\frac{\overline{Z}(\zeta)}{[\zeta \phi'(\ell) + \phi^2(\ell)][\zeta \phi'(m) + \phi^2(m)]}$$

After some manipulations we get the following expression for the truncated two body density:

$$\rho_T(\vec{r_1},\vec{r_2}) = \rho(\vec{r_1},\vec{r_2}) - \rho(\vec{r_1})\rho(\vec{r_2})$$

$$= -\frac{1}{\pi^2 \Xi} \sum_{\ell,m=0}^{N-1} \frac{e^{-\alpha_1(r_1^2-R_1^2)-\alpha_2(r_2^2-R_1^2)}}{\phi'(\ell)\phi^2(m)} z_1^{\ell} z_2^{m} z_1^{*m} z_2^{*\ell} \left(\frac{r_2}{R_1}\right)^{2(\alpha_2-\alpha_1)R_1^2}$$

$$\cdot \frac{1}{2i\pi} \oint d\zeta \frac{e^{Y(\zeta)} \chi(m+1)}{[\zeta + \chi(\ell+1)][\zeta + \chi(m+1)]} \qquad (3.12)$$

In the plane surface limit, again by the method of steepest descents we obtain

$$\rho_T(x_1, x_2, y) = -\frac{1}{\pi^2} z_0 \lim_{R_1 \to \infty} \left| \sum_{n=0}^{\infty} \frac{e^{-\frac{1}{2}\alpha_1(r_1^2 - R_1^2) - \frac{1}{2}\alpha_2(r_2^2 - R_1^2)} z_1^n z_2^{n+n_2}}{R_1^{(n_2-n)} [z_0 \varphi'(n) + \varphi^2(n)]} \right|^2 \qquad (3.13)$$

where z_0 is the same saddle point as before. Using the expression (2.12) for the incomplete gamma function, and replacing the sum by an integral over t, we find

$$\rho_T(x_1, x_2, y) = -\frac{4\alpha_1}{\pi^3} z_0 \, e^{-2(\alpha_1 x_1^2 + \alpha_2 x_2^2)} \left| \int_{-\infty}^{+\infty} \frac{e^{-t(x_1 + x_2 - iy)\sqrt{2\alpha_1}}}{z_0 \, \text{erfc}(-t) e^{t^2} + m \, e^{m^2 t^2} \text{erfc}(mt)} \right|^2 \qquad (3.14)$$

where $y = y_1 - y_2$. In the general case we have

$$\rho_T(x_1, x_2, y) = -g(x_1) g(x_2) \left| \frac{2\alpha_1}{\pi^{3/2}} \int_{-\infty}^{+\infty} dt \, \frac{e^{-t(x_1 + x_2 - iy)\sqrt{2\alpha_1}}}{z_0 \, \text{erfc}(-t) e^{t^2} + m \, e^{m^2 t^2} \text{erfc}(mt)} \right|^2 \qquad (3.15)$$

where $g(x)$ is given by (3.6).

This result becomes identical to the one for the permeable membrane[10,

when $z_0 = 1$. By an analysis similar to that of Jancovici [8,10] we can see that in the exact solution there will be no long ranged correlations along the interface: ρ_T decays exponentially as a function of y. In the MFA however the pair correlation function along the interface will decay only as y^{-2} because in this approximation each side of the interface is like an OCP face an insulating ,charged surface [8].

Our results are in accordance with Jancovici's conjecture that short ranged decay of the pair correlation function is a general feature of the interface between two conducting media[10].

The behaviour of $\rho_T(x_1, x_2, y)$ for the same case as figure 1 is shown in figures 2,3 and 4 for different locations of the particule 2 in the RHS of the membrane. In figure 4, the correlations are almost those of the bulk phase[6]

$$\rho_T(x_1, x_2, y) \longrightarrow -\left(\frac{\alpha_2}{\pi}\right)^2 \exp\left[-\alpha_2\left[(x-x_2)^2 + y^2\right]\right] \qquad (3.16)$$

Because of the fast decay of the correlation function in all directions the correlation functions will obey the theorems concerning the nonexistence of multipoles , that is any finite size fixed multipole will be perfectly screened[16]. In appendix B we show explicitly that both the monopole and dipole sum rules are indeed satisfied.

4- POTENTIAL DROP AND DIFFERENTIAL CAPACITY

a) Potential drop

The potential drop across the interface $\Delta\varphi = \varphi(\infty) - \varphi(-\infty)$ can be calculated by computing the first moment of the charge profile

$$\Delta\varphi = 2\pi e \left[\int_{-\infty}^{0} x\left[\rho(x) - \frac{\alpha_1}{\pi}\right]dx + \int_{0}^{\infty} x\left[\rho(x) - \frac{\alpha_2}{\pi}\right]dx \right] \qquad (4.1)$$

The integration can be performed very easily for m=1, with the explicit result

$$\Delta\varphi(m=1) = -\frac{e}{2} \ln z_0 \qquad (4.2)$$

Remembering that z was introduced as the ratio of the fugacities on both sides of the interface, it is evident that there must be a relation connecting the potential drop $\Delta\varphi$ to z_0 .Indeed we have

$$z_0 = \exp\left[\beta(\mu_1 - \mu_2 - e\Delta\varphi)\right] \qquad (4.3)$$

where μ_1 and μ_2 are the chemical potentials in the two bulk phases.For m=2 one has

$$\mu_1 - \mu_2 = \frac{e^2}{4} \ln \frac{\alpha_2}{\alpha_1} \qquad (4.4)$$

hence (4.3) becomes

$$\zeta_o = m \exp(-2\Delta\varphi/e) \qquad (4.5)$$

Relations (4.3) or (4.5) reflect the fact that an impermeable membrane renders invalid the internal thermodynamic equilibrium condition

$$\mu_1 + e\,\varphi(-\infty) = \mu_2 + e\,\varphi(+\infty) \qquad (4.6)$$

In the permeable interface case (4.6) holds [17] so that necessarily $\zeta_o = 1$. This explains the results found above for the one and two body density functions.

It is now clear that our model behaves like an ideally polarizable interface. While in the permeable case the potential drop always satisfies (4.6) this is not true anymore for the present model, and $\Delta\varphi$ can be considered as an external variable: For a given value of $\Delta\varphi$, we compute the density profile from (3.4) and then, the surface charge density from the electroneutrality condition (3.10). On the contrary, in the "primitive" electrode (a plasma near a charged wall) the surface charge is the natural external variable. This is an interesting feature of this microscopic model which compares well with the experimental situation where the potential drop across the interface is fixed externally.

The approximation of section (2-b) gives the following expression for $\Delta\varphi$

$$\Delta\varphi = \Delta\varphi^\circ + \frac{1}{2}\left\{\left(\frac{K_1}{K_2}\right)^{1/2} \chi(\sigma\sqrt{2}_{1}) - \left(\frac{K_2}{K_1}\right)^{1/2} \chi^{-1}(-\sigma\sqrt{2}_{1})\right\} \qquad (4.7)$$

where $\Delta\varphi^\circ$ is the potential drop of the MFA.

$$\Delta\varphi^\circ = -\frac{e}{2}\,\ln\left[\chi(\sigma\sqrt{2}_{1})/m\right] \qquad (4.8)$$

(4.7) does not satisfy the exact relation (4.5).

Figure 5 shows the relation between the potential drop and the surface charge for the primitive electrode and for the exact solution of the full coupled model. In the scale of the figure, the MFA, approximation (2-b) and the exact solution are indiscernable. However, the potentials of zero charge are zero for the MFA ,.142 for (2-b) ,and .114 for the exact solution. For negative charges the behaviour of the primitive model is totally different from the coupled model.

b) Differential capacity.

A quantity of central interest in experimental electrochemistry is the differential capacity.This quantity has often been used to characterize the polarizable interface. It is defined by $C = \dfrac{\partial(e\Psi/\pi)}{\partial \Delta\varphi}$.

Since from (4.5)

$$\frac{\partial \sigma}{\partial \Delta\varphi} = -\frac{2m}{c}\,\zeta_0\,\frac{\partial \sigma}{\partial \zeta_0} \qquad (4.9)$$

we can calculate C as a function of ζ_0 and hence as a function of the potential drop $\Delta\varphi$.Using the electroneutrality relation (3.10) and (3.4) we find

$$C(\Delta\varphi) = \frac{\zeta_0}{\pi}\sqrt{2\alpha_1}\int_{-\infty}^{+\infty}\frac{\chi(t)}{[\zeta_0 + \chi(t)]^2}\,dt \qquad (4.10)$$

For m=1 and $\Delta\varphi = 0$ ($\zeta_0 = 1$), the integral can be performed explicitly and gives

$$C_{m=1}(\Delta\varphi = 0) = \frac{\sqrt{2\alpha}}{4\pi}\int_{-\infty}^{+\infty}[erfc(t)]^2 dt = \frac{\sqrt{\alpha}}{\pi^{3/2}} \qquad (4.11)$$

In figure 6 we show the dependence of C with the potential.It is amusing to note that the shape of the curve has a hump instead of the usual dip of the theory of the diffuse layer [18,19].This hump is present in many experimental curves, and has generated considerable controversy about its origin.The explanation of the hump in our model is based on the fact that because the two sides of the interface have always opposite charges,the mobile ions on one of those sides are pushed away from the interface.The distance between the center of the excess charges of the positive and negative sides of the interface will increase with the charge (or the potential).The capacity is therefore maximum when this distance is smallest,which occurs near (but not exactly,except in the case m=1) the point of zero charge (p.z.c).

In the MPA the capacity curve has this same qualitative behaviour,but notice that this effect does not exist in the primitive electrode (C->∞ for $\Delta\varphi$->-∞).

5- THERMODYNAMICS AND SUM RULES

In the particular geometry of our model, the excess Helmholtz free energy of the system can be separated , for large R_1 , into a bulk contribution which is proportional to R_1^2 , and a surface contribution which grows as R_1

$$F_{exc} = \pi R_1^2 f_{exc}^b + 2\pi R_1 f_{\cdot}^s + O(1/R_1) \qquad (5.1)$$

where

$$f_{exc}^b = \lim_{R_1 \to \infty} \frac{F_{exc}}{\pi R_1^2}$$

and

$$f^s = \lim_{R_1 \to \infty} \frac{F_{exc} - \pi R_1^2 f_{exc}^b}{2\pi R_1}$$

In the MFA the surface excess free energy is

$$f_o^s = f_1^s + f_2^s \qquad \qquad (5.2)$$

where [14]

$$f_i^s = \frac{\sigma_i}{\pi}\mu_i - \frac{e^2}{4\pi}\left[\sigma_i^2 + \frac{4}{3}\frac{\sigma_i^3}{\alpha_i} + \sqrt{2\alpha_i}\int_{-\infty}^{\sigma_i\sqrt{2/\alpha_i}} dt \ \ln\left[\frac{erfc(t)}{2}\right]\right] \qquad (5.3)$$

$$i = 1,2 \quad \text{and} \quad \sigma_i = (-1)^i \sigma$$

(In [14] the first term of the right hand side of (5.3) does not exist because Smith considers the excess free energy caused by the increase of the surface charge density from 0 to σ/π , while keeping the number of particles constant)

For the coupled system we have

$$f^s = f_o^s + \Delta f^s \qquad (5.4)$$

where Δf^s is given by (2.37) .

a) Surface tension and Lippmann's equation

Consider now the derivative of the surface energy with respect to

the surface charge density $\dfrac{\partial f^s}{\partial(\sigma/n)}$.

From [14], we know that

$$\frac{\partial f_0^s}{\partial(\sigma/n)} = \mu_2 - \mu_1 + e\,\Delta\varphi^0 \qquad (5.5)$$

where $\Delta\varphi^0$ is the potential drop in the MFA, given by (4.8).

For a charged fluid in the presence of a charged hard wall, relation (5.5) is merely a consequence of the linearity of the Hamiltonian in the external field due to the charge density on the wall [14,20]

$$H(E) = H(E=0) + E\sum_i e\,x_i \qquad +\text{background term} \qquad (5.6)$$

For our model eq.(5.6) is not an exact one because we are ignoring fluctuation terms due to correlations of charge distributions across the interface. Indeed (5.6) is the MFA Hamiltonian.

Now, from (2.37) we have

$$\frac{\partial \Delta f^s}{\partial(\sigma/n)} = -\frac{e^2}{2}\left\{ \ln\left[\frac{3_0 + \chi(\sigma\sqrt{2/4_1})}{\chi(\sigma\sqrt{2/4_1})}\right] - \ln\left[\frac{3_0 + \chi(\sigma\sqrt{2/4_1})}{3_0}\right] \right\} = \frac{e^2}{2}\ln\left[\frac{\chi(\sigma\sqrt{2/4_1})}{2}\right]$$

$$(5.7)$$

where we have used (2.34) to eliminate $\dfrac{\partial 3_0}{\partial\sigma}$.

Hence

$$\frac{\partial f^s}{\partial(\sigma/n)} = \mu_2 - \mu_1 + e\,\Delta\varphi^0 + \frac{e^2}{2}\ln\left[\frac{\chi(\sigma\sqrt{2/4_1})}{2}\right] = \mu_2 - \mu_1 - \frac{e^2}{2}\ln(3_0/m)$$

$$(5.8)$$

and using (4.5) we get finally

$$\frac{\partial f^s}{\partial(\sigma/n)} = \mu_2 - \mu_1 + e\,\Delta\varphi \qquad (5.9)$$

which is similar to (5.5),but where the free energy and ^the potential drop
are now the exact quantities,rather than approximations.
Therefore,the fluctuation terms neglected in (5.6) make no contribution
to this thermodynamic relation.We remark also that for the permeable
interface,because of (4.6),eq (5.9) simply means that the system adjusts
to minimize its surface free energy.

   As shown elsewhere in [21] a relation of the kind of (5.9)
implies the Lippmann equation of electrochemistry [18].

   Consider the interfacial tension γ of our system,defined by

$$\gamma = \left(\frac{\partial F_{exc}}{\partial A}\right)_{\mu_i,T,U,Q} \qquad (5.10)$$

where U is the volume of the system,A is the area of the interface,and Q
the surface charge ($Q = e\sigma A$).We have the following relation between γ and f^s

$$\gamma = f^s + \frac{\sigma}{\pi}(\mu_1 - \mu_2) - \frac{e\sigma}{\pi}\Delta\varphi \qquad (5.11)$$

(note that γ and f^s are identical only when $\sigma = 0$).Hence

$$\frac{\partial\gamma}{\partial(\sigma/\pi)} = \frac{\partial f^s}{\partial(\sigma/\pi)} + \mu_1 - \mu_2 - e\Delta\varphi - \frac{e\sigma}{\pi}\frac{\partial\Delta\varphi}{\partial(\sigma/\pi)} = -e\frac{\sigma}{\pi}\frac{\partial\Delta\varphi}{\partial(\sigma/\pi)}$$

$$(5.12)$$

where (5.9) has been used .We finally obtain,considering $\Delta\varphi$ as our external
variable

$$\frac{\partial\gamma}{\partial\Delta\varphi} = -e\frac{\sigma}{\pi} \qquad (5.13)$$

which is the standard form of Lippmann's equation [18].

   We note that we have given here a statistical mechanical,microscopic
derivation of this equation,for this particular model.The usual
proof of this equation involves only thermodynamic arguments,although
there have been recently several attempts of microscopic derivations [12,22-24]

Quite surprisingly it can be shown analytically,that the approximate surface free energy (2.40) also verifies Lippmann's equation.

Figure 7 shows the dependence of the surface tension calculated from (5.4) and (5.11) with the applied potential.This curve is known to the electrochemists as the electrocapillarity curve.As in the case of the differential capacity,this curve also mimics real systems behaviour with the characteristic inverted parabolic shape

Since Lippmann's equation implies that the surface charge is the slope of the electrocapillarity curve the point of zero charge corresponds to its maximum.

5-b) Other sum rules

For an OCP near a charged hard surface the following sum rule is true [21]

$$\frac{\partial f^s}{\partial \rho} = -e \int_0^\infty [\varphi(x) - \varphi(\infty)] \, dx \qquad (5.14)$$

where ρ is the bulk density and $\varphi(x)$ is the local electrostatic potential.

In the present model it is cléar that relation (5.14) holds for each side of the interface separately in the MFA. We show in appendix C that it is also true for the exact solution.Hence we have

$$\begin{cases} \dfrac{\partial f^s}{\partial \alpha_1} = e^2 \int_{-\infty}^0 x^2 \, [\rho(x) - \frac{\alpha_1}{\pi}] \, dx \\[4mm] \dfrac{\partial f^s}{\partial \alpha_2} = e^2 \int_0^\infty x^2 \, [\rho(x) - \frac{\alpha_2}{\pi}] \, dx \end{cases} \qquad (5.15)$$

where we have used Poisson's equation.These are new sum rules for this model involving the second moment of the charge density distribution.

These relations are also valid for the case of the permeable interface.

When m=1 ($\alpha_1 = \alpha_2 = \alpha$) we have the simple relation

$$\frac{\partial f^s}{\partial \alpha} = e^2 \int_{-\infty}^{+\infty} x^2 \left[\rho(x) - \frac{\alpha}{\pi} \right] dx \qquad (5.16)$$

A last sum rule is the so called "contact theorem". For the permeable interface it has been shown that [17]

$$P_1 - P_2 = \frac{e\alpha_1}{\pi} \left[\varphi(0) - \varphi(-\infty) \right] - \frac{e\alpha_2}{\pi} \left[\varphi(0) - \varphi(\infty) \right] \qquad (5.17)$$

where P_1 and P_2 are the bulk pressures on both sides of the interface.
The presence of the impenetrable membrane modifies this relation. We now have

$$P_1 - P_2 = \frac{e\alpha_1}{\pi} \left[\varphi(0) - \varphi(-\infty) \right] - \frac{e\alpha_2}{\pi} \left[\varphi(0) - \varphi(\infty) \right] + kT \left[\rho_1(0) - \rho_2(0) \right] \qquad (5.18)$$

as shown in appendix C. Note that the surface charge density does not appear explicitly. When m=1 (5.18) gives

$$\rho_1(0) - \rho_2(0) = -\frac{2\alpha}{\pi} \Delta\varphi / e = \frac{\alpha}{\pi} \ln \zeta_0 \qquad (5.19)$$

which is equivalent to (3.8) the equation for the jump in ion density
at the interface.

After some straightforward, but lenghty manipulations, it can be
shown that the approximate solution (2-b) has the remarkable feature
of satisfying both (5.15) and (5.18).

5-c) General derivation of the preceding sum rules.

The sum rules of the preceding section are also true for the
general ,three dimensional interface of two OCP at an arbitrary coupling .

This can be shown by an extension of the argument used elsewhere [25]

which consists in studying the variation δF of the Helmholtz free energy produced by a variation of the background density $n(\vec{r})$ or of some external one body potential $\varphi^{ext}(\vec{r})$, while holding the number of particles and the temperature fixed.

From the definition of the Helmholtz free energy we have in general

$$\delta F = \int \rho(\vec{r}) \, \delta\varphi^{ext}(\vec{r}) \, d\vec{r} \; - \; e \int \varphi(\vec{r}) \, \delta n(\vec{r}) \, d\vec{r} \qquad (5.20)$$

The second term of the RHS of (5.20) is due to the constant neutralizing background.

Consider now a system consisting of two slabs, one of background density $\frac{\alpha_1}{\pi}$ extending from $-L<x<0$, and another slab of density $\frac{\alpha_2}{\pi}$ going from $0<x<L$. Eventually we will take the limit $L \to \infty$. The impenetrable membrane is located at $x=0$ and can be represented by the external potential

$$\varphi_1^{ext}(x) = \begin{cases} +\infty & x > 0 \\ 0 & x < 0 \end{cases}$$

(5.21) for all particles of the left hand side

$$\varphi_2^{ext}(x) = \begin{cases} 0 & x > 0 \\ +\infty & x < 0 \end{cases}$$

                    for all particles of the right hand side

The electroneutrality conditions imply that

$$N_1 = \frac{A}{\pi}(\alpha_1 L - \sigma)$$

$$N_2 = \frac{A}{\pi}(\alpha_2 L + \sigma)$$

$$(5.22)$$

where A is the area of the interface.

Consider now the variation δF in the free energy when the position of the impenetrable wall is displaced by an infinitesimal distance δL

while holding A, N_1, N_2, σ and T at a fixed value.

The left hand side now goes from $-L$ to δL and has background density $\frac{1}{\pi}(\alpha_1 + \delta\alpha_1)$

The right hand side extends from L to L and has density $\frac{1}{\pi}(\alpha_2 - \delta\alpha_2)$

Since $A, N_1, N_2,$ and σ are constant, we have

$$\alpha_1 \, \delta L + \delta\alpha_1 \, L = \alpha_2 \, \delta L - \delta\alpha_2 \, L = 0 \qquad (5.23)$$

and the volumes of each side of the interface change by the amount

$$\delta U_1 = -\delta U_2 = A \, \delta L \qquad (5.24)$$

(5.20) becomes

$$\delta F = A \left[\int_{-\infty}^{0} \rho(x) \, \delta\varphi_1^{ext}(x) dx + \int_{0}^{\infty} \rho(x) \, \delta\varphi_2^{ext}(x) dx - e \int_{-\infty}^{+\infty} \varphi(x) \, \delta n(x) dx \right] \qquad (5.25)$$

Writing

$$\rho(x) = \begin{cases} y_1(x) \, \exp\left[-\beta \varphi_1^{ext}(x)\right] & x < 0 \\ \\ y_2(x) \, \exp\left[-\beta \varphi_2^{ext}(x)\right] & x > 0 \end{cases} \qquad (5.26)$$

and using (5.23), we find after some calculations

$$\delta F = -AkT \left[\rho_1(0) - \rho_2(0) \right] \delta L - eA \frac{\delta L}{\pi} \Big\{ \alpha_1 \left[\varphi(0) - \varphi(-\infty) \right] - \alpha_2 \left[\varphi(0) - \varphi(+\infty) \right]$$

(5.27)
$$- \frac{\alpha_1}{L} \int_{-L}^{0} \left[\varphi(x) - \varphi(-\infty) \right] dx + \frac{\alpha_2}{L} \int_{0}^{L} \left[\varphi(x) - \varphi(+\infty) \right] dx \Big\}$$

Introducing the functions $y_i(x)$ is a standard device in the theory of fluids with hard repulsive cores. The essential feature of these functions is that they must be continuous across the interface.

In equation (5.27) we see that the free energy variation has a volume and a surface contribution, which are readily identified with thermodynamic quantities:

$$\delta F = -P_1 \, \delta U_1 - P_2 \, \delta U_2 + A \, \delta f^s \qquad (5.28)$$

The presence of the surface term in (5.28) is again a manifestation of the existence of a neutralizing background. A similar term will also be present if one of the sides is a quantum mechanical jellium [26]

From (5.23) and (5.24) we get for (5.28)

$$\delta F = -A\,\delta L\,(P_1 - P_2) \;-\; A\frac{\delta L}{L}\left[\,\alpha_1\frac{\partial f^s}{\partial \alpha_1} - \alpha_2\frac{\partial f^s}{\partial \alpha_2}\,\right] \qquad (5.29)$$

Comparing the volume term of (5.27) and (5.29) we get the contact theorem (5.18). The surface term yields

$$\alpha_1\frac{\partial f^s}{\partial \alpha_1} - \alpha_2\frac{\partial f^s}{\partial \alpha_2} = -\frac{e}{\pi}\alpha_1\int_{-\infty}^{0}[\varphi(x)-\varphi(-\infty)]\,dx \;+\; \frac{e\,\alpha_2}{\pi}\int_{0}^{\infty}[\varphi(x)-\varphi(+\infty)]\,dx \qquad (5.30)$$

This relation is weaker than (5.15). We conjecture, however, that relations (5.15) and (5.16) are valid for all couplings in two and three dimensions.

6-CONCLUSIONS

In the present paper we have solved exactly in two dimensions and for a special temperature the statistical mechanics of the interface between two charged one component plasmas separated by an impermeable membrane. The interesting fact about this model is that it treats the entire double layer, the "metal" and the "electrolyte" side, on an equal footing, and it can be switched from the polarizable to nonpolarizable behaviour. The above calculations could be easily extended to more complex situations. For instance in Appendix D, the case when the membrane itself has a fixed charge density is discussed.

Another solvable case is that of several contiguous impermeable membranes separating plasmas of different charge densities.

From the microscopic point of view,an important result of this paper is that
the existence of an impermeable membrane is strictly equivalent to a step
variation in the fugacity of the mobile ions.For the permeable membrane
there is no discontinuity, and therefore the potential drop across the
interface is constant.This is perhaps the first rigorous illustration
of the fact that an ideally polarizable electrode exists only when there is
no miscibility between the two phases.

In conclusion the behaviour of this model exhibits a remarkable
ressemblance to that of real electrodes:the potential drop across the interface
is the natural external variable (and not the surface charge density)
Lippmann's equation is verified,the shape of the electrocapillarity
and capacity curves shares common features with experiment.
The remarkable fact that such widely different systems have similar
characteristic behaviour,seems to imply that they are not very sensitive to
the structural details of the interface.

APPENDIX A: ELECTRONEUTRALITY CONDITION

Consider the left hand side of the interface $(x<0)$. From (3.4) we get

$$\rho(x) - \frac{\alpha_1}{\pi} = \frac{\alpha_1}{\pi^{3/2}} \int_{-\infty}^{+\infty} e^{-(t + x\sqrt{2\alpha_1})^2} \frac{\zeta_0 \, erfc(t) - m \, e^{(m^2-1)t^2} erfc(mt)}{\zeta_0 \, erfc(-t) + m \, e^{(m^2-1)t^2} erfc(mt)} \, dt \qquad (A.1)$$

Hence

$$\int_{-\infty}^{0} \left(\rho(x) - \frac{\alpha_1}{\pi}\right) dx = \frac{\sqrt{\alpha_1}}{2\pi\sqrt{2}} \int_{-\infty}^{+\infty} erfc(-t) \frac{\zeta_0 \, erfc(t) - m \, e^{(m^2-1)t^2} erfc(mt)}{\zeta_0 \, erfc(-t) + m \, e^{(m^2-1)t^2} erfc(mt)} \, dt$$

$$= \frac{\sqrt{\alpha_1}}{2\pi\sqrt{2}} \int_{-\infty}^{+\infty} \frac{\zeta_0 \, erfc(t) - \chi(t) \, erfc(-t)}{\zeta_0 + \chi(t)} \, dt \qquad (A.2)$$

But

$$\frac{1}{2} \cdot \frac{\zeta_0 \, erfc(t) - \chi(t) \, erfc(-t)}{\zeta_0 + \chi(t)} = \frac{1}{2} \, erfc(t) - \frac{\chi(t)}{\zeta_0 + \chi(t)}$$

$$= -\frac{1}{2} \, erfc(-t) + \frac{\zeta_0}{\zeta_0 + \chi(t)} \qquad (A.3)$$

Hence

$$\int_{-\infty}^{0} \left(\rho(x) - \frac{\alpha_1}{\pi}\right) dx = \frac{\sqrt{\alpha_1}}{\pi\sqrt{2}} \left\{ \int_{-\infty}^{\sigma\sqrt{2\alpha_1}} \left[-\frac{1}{2} erfc(-t) + \frac{\zeta_0}{\zeta_0 + \chi(t)} \right] dt + \int_{\sigma\sqrt{2\alpha_1}}^{\infty} \left[\frac{1}{2} erfc(t) - \frac{\chi(t)}{\zeta_0 + \chi(t)} \right] dt \right\}$$

$$= \frac{\sqrt{\alpha_1}}{\pi\sqrt{2}} \left\{ -\sigma\sqrt{\tfrac{2}{\alpha_1}} + \int_{-\infty}^{\sigma\sqrt{2\alpha_1}} \frac{\zeta_0}{\chi(t) + \zeta_0} \, dt - \int_{\sigma\sqrt{2\alpha_1}}^{\infty} \frac{\chi(t)}{\zeta_0 + \chi(t)} \, dt \right\} \qquad (A.4)$$

Then, using (2.34) we readily obtain the electroneutrality relation (3.10). The procedure is analogous for $x>0$.

APPENDIX B: MULTIPOLE SUM RULES

The first and second multipole sum rules are

$$\int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dy\; \rho_T(x_1, x_2, y) = -\rho(x_1) \qquad (B.1)$$

and

$$\int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dy\; (x_2 - x_1)\, \rho_T(x_1, x_2, y) = 0 \qquad (B.2)$$

Consider first (3.1)

From (3.15) we have

$$I_1 = \int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dy\; \rho_T(x_1, x_2, y) = -\frac{4\alpha_1^2}{\pi^3} g(x_1) \int_{-\infty}^{+\infty} dx_2\; g(x_2) \int dt_1\, dt_2\; R(t_1) R(t_2) \int_{-\infty}^{+\infty} dy\; e^{i y \sqrt{2\alpha_1} (t_1 - t_2)}$$

$$= -\frac{8\alpha_1^2}{\sqrt{2\alpha_1}\, \pi^2} g(x_1) \int_{-\infty}^{+\infty} dx_2\; g(x_2) \int_{-\infty}^{\infty} dt\; R(t)^2 \qquad (B.3)$$

where

$$R(t) = \frac{e^{-t(x_1 + x_2)\sqrt{2\alpha_1}}}{3_0\, \mathrm{erfc}(-t)e^{t^2} + m e^{m^2 t^2}\, \mathrm{erfc}(mt)}$$

Hence

$$I_1 = -\frac{8\alpha_1^2}{\sqrt{2\alpha_1}\, \pi^2} g(x_1) \int_{-\infty}^{\infty} dt\; \frac{e^{-2t x_1 \sqrt{2\alpha_1}}}{[3_0\, \mathrm{erfc}(t)e^{t^2} + m e^{m^2 t^2}\, \mathrm{erfc}(mt)]^2} \left\{ 3_0 \int_{-\infty}^{0} dx_2\; e^{-2\alpha_1 x_2^2 - 2t x_2 \sqrt{2\alpha_1}} \right.$$
$$\left. + \int_{0}^{\infty} dx_2\; e^{-2\alpha_2 x_2^2 - 2t x_2 \sqrt{2\alpha_1}} \right\} \qquad (B.4)$$

Performing the last integration we find (B.1).

Consider now (3.2), which, by use of (B.1) can be rewritten

$$I_2 = \int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dy\; x_2\, \rho_T(x_1, x_2, y) = -x_1 \rho(x_1) \qquad (B.5)$$

We have

$$I_2 = -\frac{8\alpha_1^2}{\pi^2\sqrt{2\alpha_1}}\, g(x_1) \int_{-\infty}^{+\infty} dx_2\, x_2\, g(x_2) \int_{-\infty}^{+\infty} dt\, R^2(t) \qquad (B.6)$$

$$= -\frac{8\alpha_1^2}{\pi^2\sqrt{2\alpha_1}}\, g(x_1) \int_{-\infty}^{+\infty} dt\, \frac{e^{-2t x_1\sqrt{2\alpha_1}}}{[\, z_0\, \mathrm{erfc}(t) e^{t^2} + m\, e^{m^2 t^2}\, \mathrm{erfc}(mt)\,]^2} \left[z_0\, e^{t^2} \int_{-\infty}^{0} dx_2\, x_2\, e^{-2\alpha_1 (x_2 + \frac{t}{\sqrt{2\alpha_1}})^2} \right.$$

$$\left. + e^{m^2 t^2} \int_{0}^{\infty} dx_2\, x_2\, e^{-2\alpha_2 (x_2 + \frac{t}{\alpha_2}\sqrt{\frac{\alpha_1}{2}})^2} \right]$$

The last term between brackets is the derivative of the denominator.
Integration by parts finally yields (B.5).

APPENDIX C: VERIFICATION OF SUM RULES

We first consider the sum rule

$$\frac{\partial f^s}{\partial \alpha_2} = e^2 \int_0^\infty x^2 \left[\rho(x) - \frac{\alpha_2}{\pi} \right] dx \qquad (C-1)$$

from (3.4) we get

$$J = e^2 \int_0^\infty x^2 \left[\rho(x) - \frac{\alpha_2}{\pi} \right] dx$$

$$= \frac{e^2}{8\alpha_2 \pi} \sqrt{\frac{\alpha_1}{2}} \int_{-\infty}^{+\infty} dt \left[\operatorname{erfc}(mt)(1+2m^2t^2) - \frac{2}{\sqrt{\pi}} mt e^{-m^2 t^2} \right] \frac{m \operatorname{erfc}(mt) e^{(m^2-1)t^2} - \frac{2}{3_0} \operatorname{erfc}(-t)}{m \operatorname{erfc}(mt) e^{(m^2-1)t^2} + 3_0 \operatorname{erfc}(-t)} \qquad (C.2)$$

which can be written

$$J = \frac{e^2}{8\alpha_2 \pi} \sqrt{\frac{\alpha_1}{2}} \int_{-\infty}^{+\infty} dt \left[\operatorname{erfc}(mt)(1+2m^2t^2) - \frac{2}{\sqrt{\pi}} mt e^{-m^2 t^2} \right] \left[\frac{2m e^{(m^2-1)t^2}}{m \operatorname{erfc}(mt) e^{(m^2-1)t^2} + 3_0 \operatorname{erfc}(-t)} - 1 \right] \qquad (C.3)$$

Now we split the domain of integration in the two intervals
$[-\infty, \sigma\sqrt{2/\alpha_1}], [\sigma\sqrt{2/\alpha_1}, \infty]$, and we regroup the terms to insure convergence
when $t \to -\infty$. This yields

$$J = \frac{e^2}{4\pi \alpha_2^{3/2}} \frac{\alpha_1}{\sqrt{2}} \left\{ \int_{-\infty}^{\sigma\sqrt{2/\alpha_1}} dt \left[\frac{\operatorname{erfc}(mt)(1+2m^2t^2) e^{(m^2-1)t^2} - \frac{2}{\sqrt{\pi}} mt e^{-t^2}}{m \operatorname{erfc}(mt) e^{(m^2-1)t^2} + 3_0 \operatorname{erfc}(-t)} - \frac{1}{m} - 2mt^2 \right] \right.$$

$$\left. + \int_{\sigma\sqrt{2/\alpha_1}}^\infty dt \frac{\operatorname{erfc}(mt)(1+2m^2t^2) e^{(m^2-1)t^2} - \frac{2}{\sqrt{\pi}} mt e^{-t^2}}{m \operatorname{erfc}(mt) e^{(m^2-1)t^2} + 3_0 \operatorname{erfc}(-t)} \right\} + \frac{e^2 \sigma}{4\pi \alpha_2} \left(1 + \frac{4}{3} \frac{\sigma^2}{\alpha_2} \right) \qquad (C.4)$$

Using the relations (2.37), (5.3) and (5.4), which define f^s and
the saddle point equation (2.34) to eliminate $\frac{\partial 3_0}{\partial \alpha_2}$, it is easy to
see that (C.4) is nothing but $\frac{\partial f^s}{\partial \alpha_2}$.

The calculation is similar for the left hand side and also for the
symmetric case $m=1$.

We verify now contact the theorem (5.18):

From (3.4) we have

$$\frac{e^2\alpha_1}{\pi}[\varphi(0) - \varphi(-\infty)] = 2e^2\alpha_1 \int_{-\infty}^{0} x[\rho(x) - \frac{\alpha_1}{\pi}]dx \qquad (C.5)$$

$$= \frac{e^2\alpha_1}{2\pi} \int_{-\infty}^{+\infty} [t\, \text{erfc}(-t) + \frac{e^{-t^2}}{\sqrt{\pi}}] \, \frac{m\, e^{(m^2-1)t^2}\, \text{erfc}(mt) - z_0\, \text{erfc}(t)}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)} \, dt$$

$$= \frac{e^2\alpha_1}{2\pi} \int_{-\infty}^{+\infty} [t\, \text{erfc}(-t) + \frac{e^{-t^2}}{\sqrt{\pi}}] [1 - \frac{2z_0}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)}] \, dt$$

which can be written

$$\frac{e^2\alpha_1}{\pi}[\varphi(0) - \varphi(-\infty)] = \frac{e^2\alpha_1}{2\pi} - \frac{e^2\alpha_1}{\pi^{3/2}} z_0 \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)} \, dt$$

$$+ \frac{e^2\alpha_1}{2\pi} \int_{-\infty}^{+\infty} t\, \text{erfc}(-t) [1 - \frac{2z_0}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)}] \, dt \qquad (C.6)$$

After similar manipulations, we get

$$\frac{e^2\alpha_2}{\pi}[\varphi(0) - \varphi(+\infty)] = -2e^2\alpha_2 \int_{0}^{\infty} x[\rho(x) - \frac{\alpha_2}{\pi}]dx$$

$$= \frac{e^2\alpha_2}{2\pi} - \frac{e^2\alpha_1}{\pi^{1/2}} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)} \, dt$$

$$+ \frac{e^2\alpha_1}{2\pi} \int_{-\infty}^{+\infty} t\, \text{erfc}(mt) [\frac{2m\, e^{(m^2-1)t^2}}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)} - 1] \, dt \qquad (C.7)$$

Hence we have

$$\frac{e^2\alpha_1}{\pi}[\varphi(0) - \varphi(-\infty)] - \frac{e^2\alpha_2}{\pi}[\varphi(0) - \varphi(\infty)] = \frac{e^2}{4\pi}(\alpha_1 - \alpha_2)$$

$$- \frac{e^2\alpha_1}{\pi^{3/2}}(z_0 - 1) \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{m\, \text{erfc}(mt)\, e^{(m^2-1)t^2} + z_0\, \text{erfc}(-t)} \, dt$$

$$(C.8)$$

where we have used

$$\int_{-\infty}^{+\infty} t \left[\operatorname{erfc}(mt) + \operatorname{erfc}(t) - 1 \right] dt = \frac{1}{2}\left(1 - \frac{\alpha_2}{\alpha_1}\right) \qquad (C.9)$$

But from (3.4) we have also

$$kT\left[\rho_1(0) - \rho_2(0)\right] = \frac{\alpha_1 e^2}{\pi^{3/2}}(z_o - 1)\int_{-\infty}^{+\infty} \frac{e^{-t^2}}{m\,\operatorname{erfc}(mt)\,e^{(m^2-1)t^2} + z_o\,\operatorname{erfc}(-t)}\,dt \qquad (C.10)$$

Adding (C.8) and (C.10) we finally recover the contact theorem (5.18)
$$\left(p = \frac{e^2}{4}\rho \ \text{for} \ \nu = 2 \right)$$

APPENDIX D: CHARGED MEMBRANE

The model proposed in this paper can be extended easily to the case where there are fixed charge distributions on each side of the interface.

Consider, for instance, the case of two charged rings, one of radius $R_1 - \varepsilon$ and surface charge density $e\sigma_1/\pi$, and the other of radius $R_1 + \varepsilon$ and surface charge density $e\sigma_2/\pi$.

Let $\varepsilon \to 0$. This is equivalent to say that the impermeable membrane has now a charge density $\quad e\dfrac{\sigma}{\pi} = \dfrac{e}{\pi}(\sigma_1 + \sigma_2)$

The calculation follows the same line as before with only some minor changes (see also [11]). The electroneutrality conditions (2.1) and (2.2) become

$$N_1 = \alpha_1 R_1^2 - \sigma_1 R_1$$
$$N_2 = (R_2^2 - R_1^2)\alpha_2 - \sigma_2 R_1 \tag{D.1}$$

and there is an extra term

$$V' = -e^2 \sigma R_1 \sum_{i=N_1+1}^{N} \ln\left(\frac{r_i}{R_1}\right)^2 \tag{D.2}$$

in the expression (2.3) of the potential energy.
In (2.6) we now have

$$n_2 = n + (\alpha_2 - \alpha_1)R_1^2 + 2\sigma R_1 \tag{D.3}$$

and

$$X(t) = m\, e^{(mt - \sigma\sqrt{2/\alpha_2})^2 - t^2}\ \frac{\mathrm{erfc}\,(mt - \sigma\sqrt{2/\alpha_2})}{\mathrm{erfc}(-t)} \tag{D.4}$$

instead of (2.13).

Furthermore we now have $\frac{1}{2}\sigma_1$ instead of σ , in all the integrals over t. For instance, the saddle point equation (2.34) reads

$$\int_{\sigma_1/\sqrt{2d_1}}^{\infty} \frac{\chi(t)}{\chi(t) + \zeta_0} \, dt = \int_{-\sigma_1/\sqrt{2d_1}}^{\infty} \frac{\zeta_0}{\chi(-t) + \zeta_0} \, dt \qquad (D.5)$$

and ζ_0 is now a function of σ_1 and σ_2 (and not only of σ)
The one and two body distribution functions are still given respectively by (3.4) and (3.15) and all the sum rules hold.

Contrary to the case of the permeable interface [11], the potential drop $\Delta\varphi$ across the interface, depends on the distribution of charges at the interface: the surface charge distributions of the interface are not screened anymore.

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FIGURE CAPTIONS

Figure 1:Density profile for $m=0.5$ and $\alpha=-1$. Units are $e=q_1=1$. $\left(\zeta_0 = 4.212\right)$

Figure 2:Level curves of the two body truncated density correlation function. Same case as Figure 1. Particle 2 is at the wall on the RHS.

Figure 3:Same as figure 2. Particle 2 has coordinates $(.5,0)$.

Figure 4:Same as figure 2. Particle 2 has coordinates $(1,0)$.

Figure 5:Potential drop versus surface charge density. The primitive electrode is compared to the full coupled model. $(m=.5)$

Figure 6:Differential capacity versus potential drop. Comparison of the primitive electrode to the full coupled model. $(m=.5)$
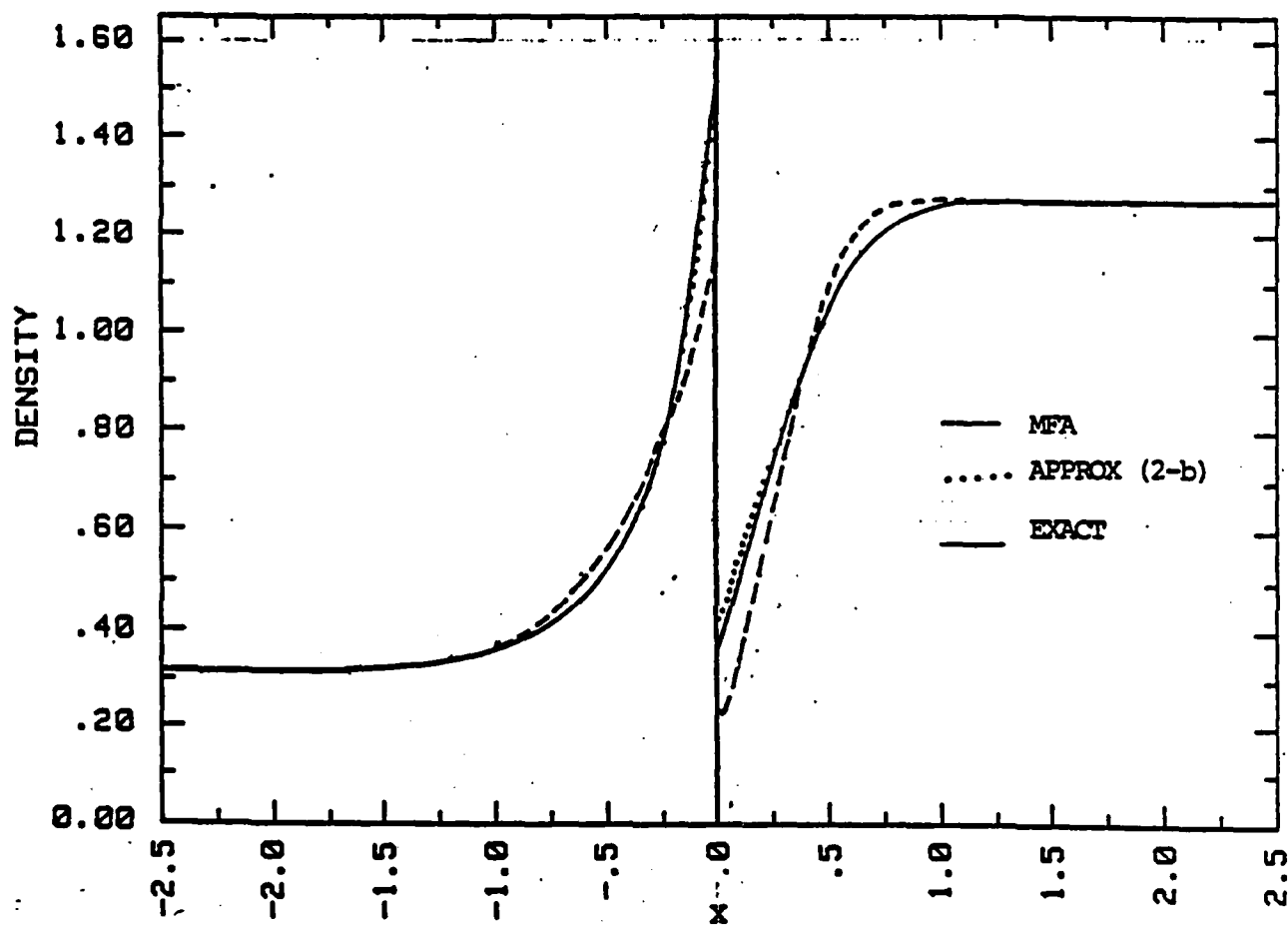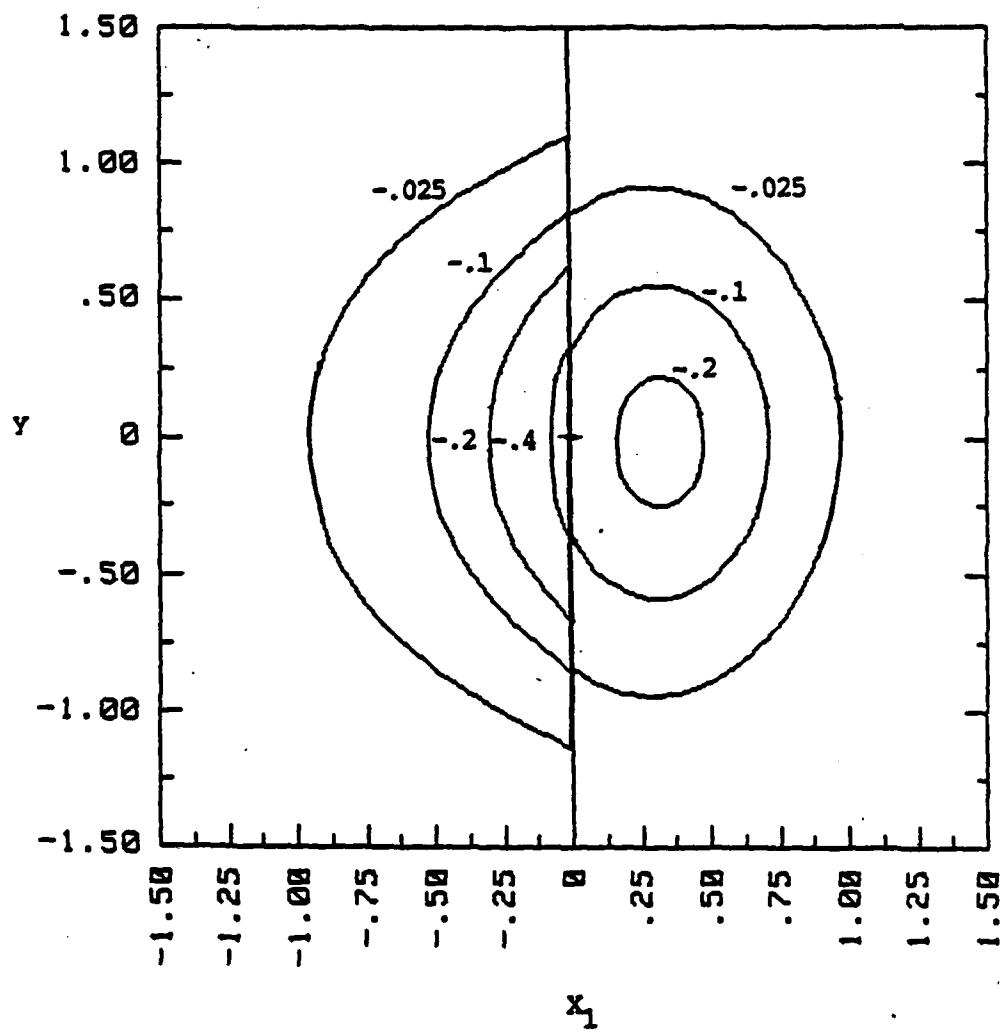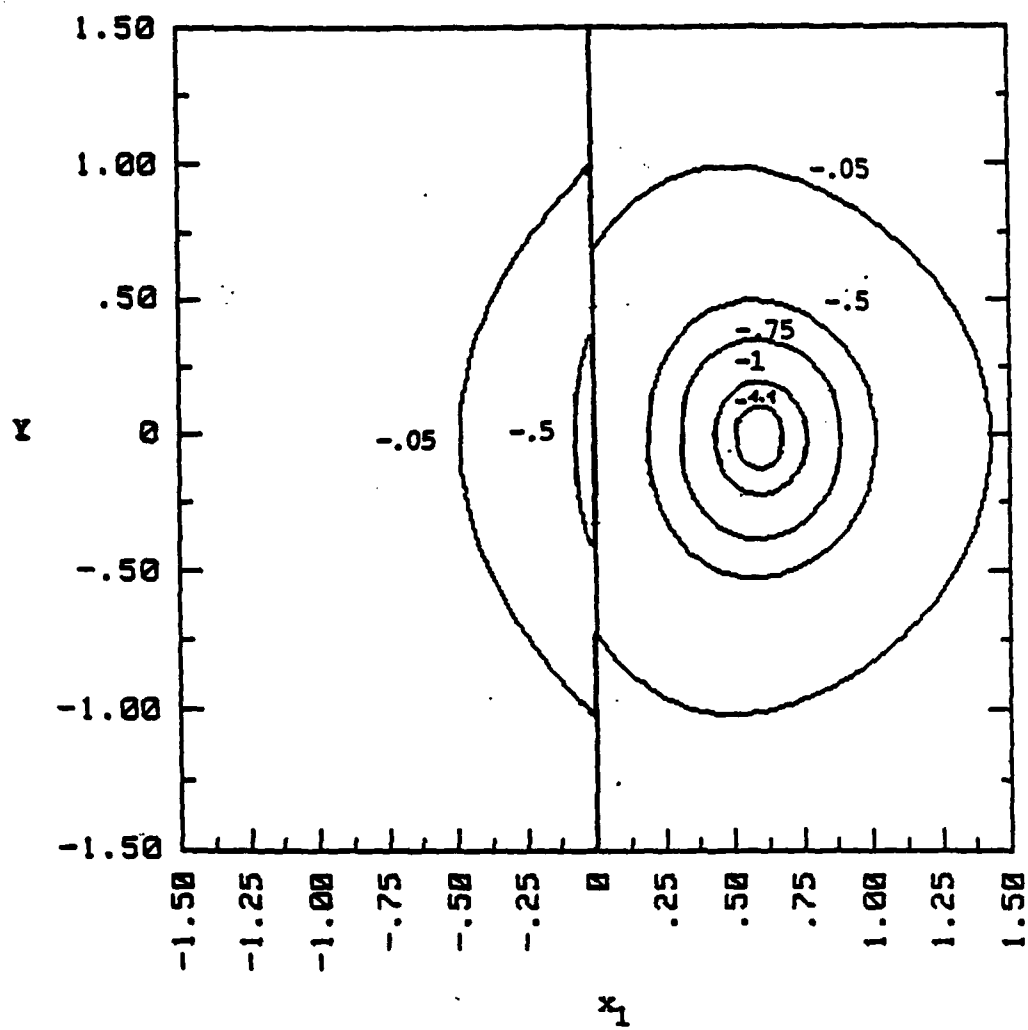
Figure 7:Electrocapilarity curve. $(m=.5)$. $\left(p.z.c. = .114\right)$

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

POTENTIAL Δφ

SURFACE CHARGE σ

——— PRIMITIVE ELECTRODE

——— COUPLED MODEL

FIGURE 5

FIGURE 6

CAPACITY

.45

.30

.15

0.00

—— PRIMITIVE ELECTRODE

—— COUPLED MODEL (EXACT)

.... COUPLED MODEL (MFA)

POTENTIAL DROP $\Delta \varphi$

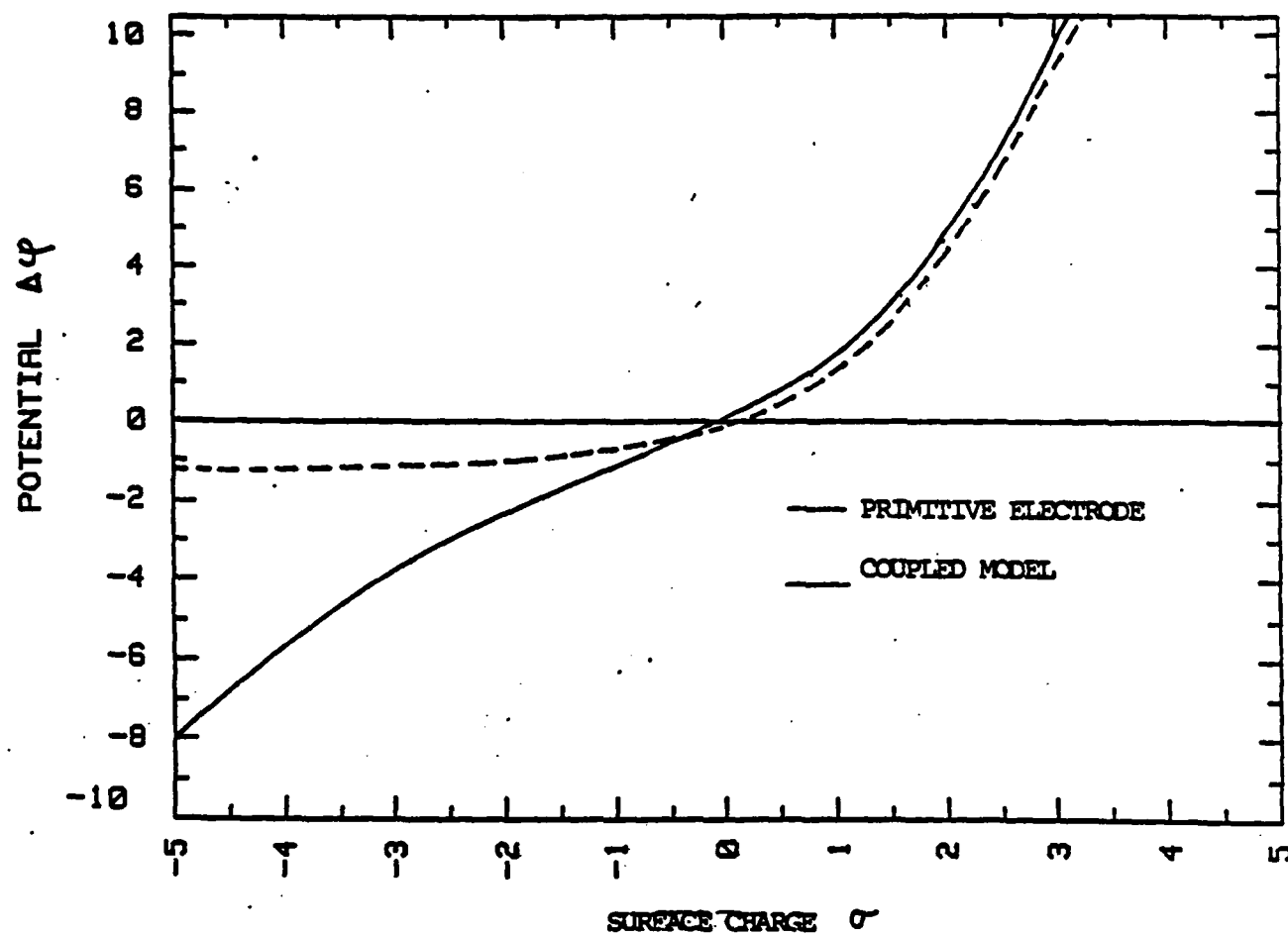-10 -9.0 -8.0 -7.0 -6.0 -5.0 -4.0 -3.0 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
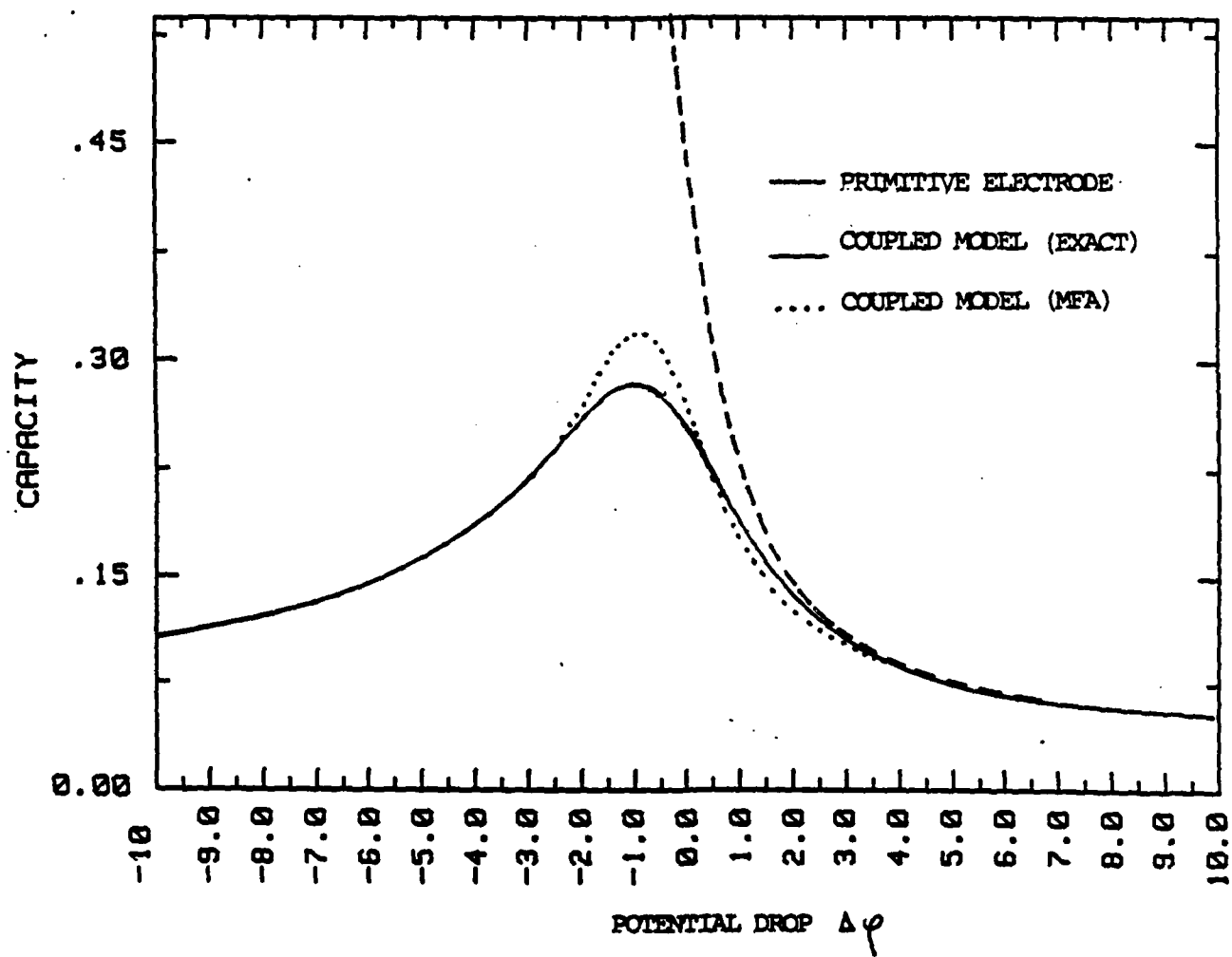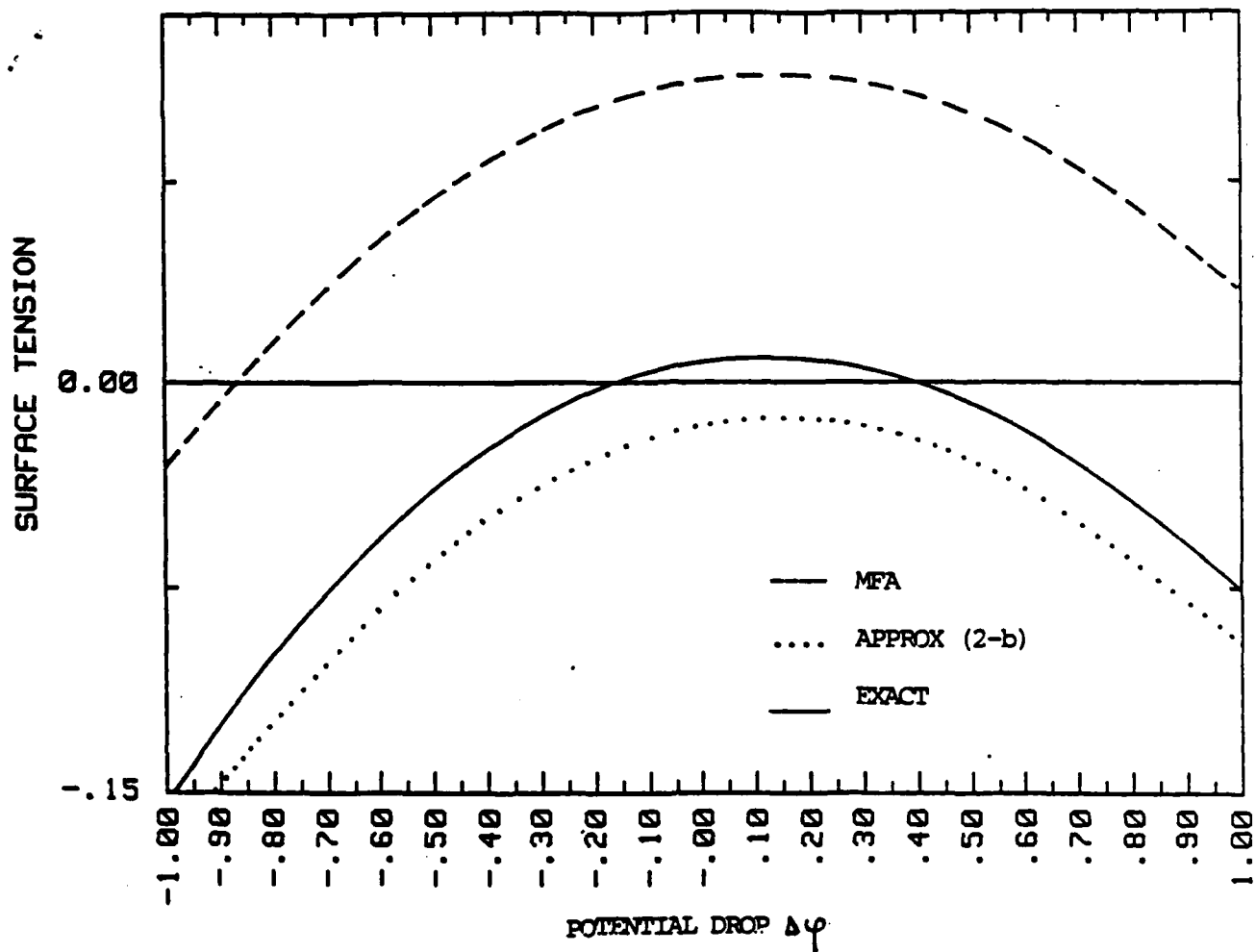
FIGURE 7

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A MICROSCOPIC MODEL FOR THE LIQUID METAL–IONIC SOLUTION INTERFACE

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ABSTRACT

A microscopic model for the metal–solution interface is presented, which, for the first time, includes both a non-ideal treatment of the metal and a molecular model for the solution side. The metal is described by a jellium model including electron–ion pseudo-potential. The solution is treated as a mixture of hard spheres with point dipoles (solvent molecules) or point charges (ions). The statistical mechanics is solved using mean spherical approximation. No a priori separation is introduced between compact and diffuse layers. A simplified version of the model is applied to the case of Hg–DMSO systems.

INTRODUCTION

The classical theories of the ideal polarized electrode are based on two premisses:

(1) The metal has no direct effect on the differential capacitance C, although it does determine the potential of zero charge and affects the orientation of solvent molecules. From an electrostatic viewpoint, every metal acts in just the same way, the only interaction being that of ideal images.

(2) The solution side has two layers: the external, or diffuse layer, which can be described by such simple models as the Gouy–Chapman (GC) theory, and the internal, or compact layer, which in the absence of specific adsorption is formed only by solvent molecules.

These two premisses are now being challenged. The recent important progress in the theory of metals and metal surfaces makes it difficult to admit that the metal is totally unresponsive to changes in the electrolyte. The surface charge distribution in the metal must respond to local changes in the electrostatic field produced by modifications in the ionic and solvent distributions. This will surely produce

254

contributions to the differential capacitance that will be different for each metal, since the response to an external field is different for each metal, and depends on details of the electronic structure near the surface. In previous work [1-3] an estimate of these effects was given. The solution side was represented by a layer of dielectric material. In a recent publication, W. Schmickler [4] has discussed a similar model. His conclusions about the role of the metal are similar to ours.

On the solution side, recent advances in the treatment of molecular solutions [5,6], i.e. solutions in which the solvent is not treated as a continuum, have made it possible to treat the statistical mechanics of the solution side of the electrode interface. Although the approach, in principle, can handle realistic models of solvents and ions, the initial work has dealt with a model in which the solvent is represented by hard spheres with point dipoles [7]. This work has revealed two important deficiencies of the classical treatment:

(1) The separation of the inner and outer layers for the solvent orientation process (or better polarization) implies a violation of Maxwell's equations. The dipoles of the solvent are oriented wherever there is an electric field, i.e., throughout the entire electric double layer.

(2) The use of local dielectric constants is also unwarranted. Although this is a much more subtle problem, recent theoretical work [8] has shown that dielectric constants have a clear meaning only for large systems (thermodynamic limit) and not at the molecular level. The polarization is the local variable that is required.

In this work we present a comprehensive theory in which all of these concepts are included. In section (I) we review the models of the metal and solution sides of the interface. The potential drop and capacitance are then computed using a simple GMSA (generalized mean spherical approximation)-based model which has the obvious advantages of analyticity and simplicity.

In section (II) we discuss the electronic density profile of this model. We then consider a model in which the physical parameters are those of an alkali-ion in DMSO in the neighbourhood of a mercury electrode.

In our model the point of zero charge is not the point of zero potential (which is the case in the restricted primitive model); we also discuss the change in the surface potential of the metal induced by the presence of the solution. The influence of some of the parameters, and detailed comparison between Hg and Ga electrodes, will be discussed in future work.

In section (V) we examine possible improvements in our work.

(I) MODEL FOR SURFACE INTERACTIONS

Consider a plane, ideally smooth electrode, where z is the distance from the metal surface. The bulk metal is then given when $z \rightarrow -\infty$. For the metal we use a jellium model (with inclusion of the electron-ion pseudo-potential). The details are given in ref. 9, but for completeness we will give an outline of this work. The metal ions are taken as a continuum of density ρ for $z < 0$. In other words

$$\rho(z) = \rho\theta(-z)$$

where $\theta(x)$ is the Heaviside function

$$\theta(x) = 1 \qquad x > 0$$

$$\theta(x) = 0 \qquad x < 0$$

The electronic gas is free to move, but its equilibrium distribution $n(z)$ will be that which minimizes the total surface energy of the system. The electron-ionic background interaction is given by a pseudo-potential. The properties of the electron gas, such as the kinetic, exchange and correlation energies are computed using the local approximation.

On the solution side the ions are represented by hard spheres of diameter σ_i and charge $\pm e$ *, and bulk density ρ_i. The solvent is also represented by hard spheres of diameter σ_d, point dipole μ and density ρ_d.

We assume that no chemical reaction can take place, and no miscibility occurs between the phases [10]. However, this model does not exclude the existence of a surface layer in which all the particles are present. In fact, the existence of this layer is consistent with contemporary theories of the metallic surfaces. Any model which does not include this layer leads to predictions which are incompatible with experiments [1,11].

In our model, the electrons can diffuse into the ionic solution. In actual practice, calculations show that both in the interface with the vacuum [12], or with a dielectric film [9], the electron density spill-over is very small. However, the change in the spill-over with the electrode charge will give a direct contribution of the metal to the differential capacitance [1,4].

The metal electrons in the solution are subject to electrostatic interactions (electron-ion and electron-dipole) but also to a repulsion due to the core electrons of ions and solvent molecules. These are represented by the Harrison repulsive potential [9].

There are several parameters in our model that are fixed a priori, but which should come out of a first-principles calculation. One of these quantities is the distance of closest approach of the ions and solvent to the plane $z = 0$ (the metal surface). We will assume that it is just the sum of the molecular radius of the solvent or ions (which for this simple model are considered to be equal) and the radius of the metallic ion. In reality, this parameter should arise from a self-consistent density functional calculation [13].

In short, we will assume that there is an ideally smooth wall, located at $z = \delta$, which cannot be penetrated by either ions or solvent molecules. The distances of closest approach are

$$z_{ion} = \delta + \sigma_i/2 \qquad \text{for ions}$$

$$z_{mol} = \delta + \sigma_d/2 \qquad \text{for solvent molecules}$$

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* We use Bohr atomic units: e = electron charge; m = electron mass; $e = m = 1$. Bohr radius: $a_0 = 0.0529$ nm. Energy unit: 1 Hartree = 27.2 eV.

There is also the problem of surface smoothness and structure. From recent experimental evidence, it is known that certain metal surfaces are subject to structural changes during chemisorption processes. In these cases the surface overlayer changes its structure. It is quite conceivable that in an intrinsically more labile environment such as that of liquid metals, the metal overlayer would also respond structurally to changes in potential.

Furthermore, the question of surface ripples (capillary waves) at the interface, and its effects on the structure and thermodynamics of the electrode is not discussed. We hope to address these and other questions in future work.

Summarizing, the ions and dipoles in the solution are not seen simply as a hard, charged surface, but rather the sum of a charged surface (located at $\delta + \sigma/2$) and a distribution of electron density beyond the plane of closest approach.

Even this simple model is not easily amenable to a complete numerical calculation. We will, therefore, in this first communication, use a simplified theory that has the advantage of giving explicit analytic expressions for the physically relevant quantities.

(II) A SIMPLIFIED MODEL

For simplicity, we shall discuss only the restricted model in which $\sigma_i = \sigma_+ = \sigma_- = \sigma_d = \sigma$ (although not in published form, the results for $\sigma_+ = \sigma_- = \sigma_d$ are also available). We also neglect the effects of the electron density on molecules and ions in the solution. We shall leave the discussion of the validity of this assumption for the future (see also ref. 3 for a first discussion of this effect). The solution is represented by the MSA [5,6] which is only qualitatively correct. Near a charged interphase a simplified theory, valid presumably for dilute solutions, has been developed by Blum
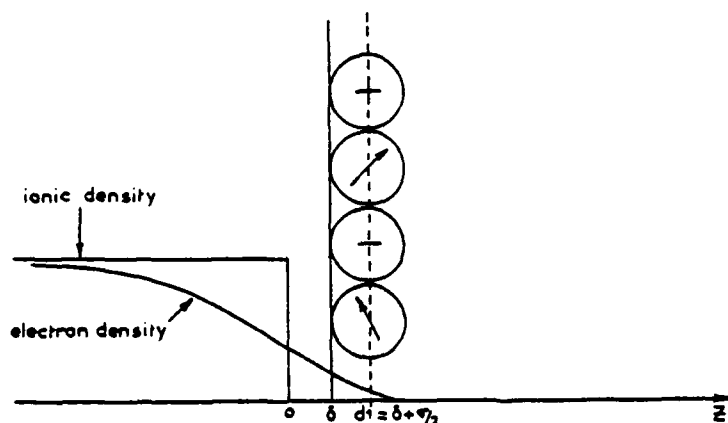

Fig. 1. Simplified model of the interface: δ = position of the ideally smooth wall; σ = diameter of the ions and solvent molecules.

and co-worker [7]. In this theory, the dipolar interactions are decoupled from the ionic distributions, which are given by the modified Gouy–Chapman (MGC) theory. We are thus satisfying the electrostatic part of the contact density theorem. The simplified model of the interface is given on Fig. 1.

The charge density profile is given by

$$q_i(z) = -\kappa q_M e^{-\kappa(z-d_1)} \tag{1}$$

where κ is Debye's inverse length and

$$d_1 = \delta + \sigma/2$$

The total excess charge of the solution side is

$$q_s = \int_{d_1}^{\infty} dz\, q_i(z) = -q_M \tag{2}$$

The electronic density profile is postulated to be of the form [1,9]

$$\begin{aligned}
n(z) &= n\left[1 - \tfrac{1}{2}e^{\alpha(z-z_0)}\right] && z < z_0 \\
&= (n/2)e^{-\alpha(z-z_0)} && z > z_0
\end{aligned} \tag{3}$$

where n is the bulk metallic electron density. Clearly, the total excess charge on the metal side is

$$q_M = \int_{-\infty}^{\infty} dz\left[\rho\theta(-z) - n(z)\right] = -nz_0 \tag{4}$$

This last relation also defines z_0.

For a given value of α, and q_M, the charge and polarization ($P(z)$) profiles are computed from the theory [7]. These in turn yield the potential $V(z)$ and electric field $E(z)$, which are obtained by solving Poisson's equation

$$\frac{\partial E(z)}{\partial z} = -\frac{\partial^2 V(z)}{\partial z^2} = 4\pi\left[\rho\theta(-z) - n(z) \right.$$
$$\left. + \theta(z - d_1)\left\{\kappa n z_0 e^{-\kappa(z-d_1)} - \frac{\partial P(z)}{\partial z}\right\}\right] \tag{5}$$

The potential $V(z)$ is continuous in all space. Because of the discontinuities in the density profiles, $V(z)$ has a different form in the regions

(I) $-\infty < z \leqslant 0$

(II) $0 < z \leqslant d_1$

(III) $d_1 < z < \infty$

The solution of eqn. (5) is straightforward, and is explained in Appendix I. The total potential drop across the interface is

$$\Delta V = V(\infty) - V(-\infty) = \frac{4\pi n}{\alpha^2}\left[\alpha z_0(\alpha d_1 - \alpha z_0) + \frac{(\alpha z_0)^2}{2} - 1\right]$$
$$+ \frac{4\pi n z_0}{\kappa} + 4\pi\int_{d_1}^{\infty} P(z)\,dz \tag{6}$$

The integral in this expression is explicitly known. The reader is referred to ref. 7 (eqn. 15) for the derivation. The result is

$$4\pi \int_{d_1}^{\infty} dz\, P(z) = \lim_{s \to 0} \tilde{P}(s)$$

The Laplace transform $\tilde{P}(s)$ is

$$\tilde{P}(s) = 4\pi \int_{d_1}^{\infty} dz\, e^{-sz} P(z) = \frac{4\pi \mu \rho_d}{\sqrt{3}} \left(\frac{\beta \mu 4\pi q_M}{\sqrt{3}} \right) \frac{1}{(\kappa + s) A(s)}$$

$$\times \frac{\beta_6^2}{\beta_3} \left\{ 1 - \frac{\kappa \sigma}{4} \frac{\beta_3}{\beta_{12}} \left[\frac{\beta_6^2}{\beta_3^2} + 2\phi_1(s) \right] \right\} \cdot e^{-sd_1} \tag{7}$$

Here ρ_d is the bulk number density of solvent molecules. The coefficients β_3, β_6 and β_{12} are functions of the bulk dielectric constant ϵ of the solvent, and are given through an auxiliary parameter λ

$$\beta_3 = \frac{3\lambda}{2+\lambda}; \qquad \beta_6 = \frac{3}{2+\lambda}; \qquad \beta_{12} = \left(\frac{3}{2} \right) \frac{1+\lambda}{2+\lambda} \tag{8}$$

The auxiliary parameter λ is computed from the equation

$$\epsilon = \lambda^2 (1+\lambda)^4 / 16 \tag{8'}$$

The functions $\phi_1(s)$ and $A(s)$ are defined by

$$\phi_1(s) = 1/(s\sigma)^2 [1 - s\sigma - e^{-s\sigma}]$$

$$A(s) = 1 - 2\phi_1(s)(\lambda^2 - 1) - 4\phi_2(s)(\lambda^2 - \lambda)$$

with

$$\phi_2(s) = \frac{1}{s\sigma} \left[\phi_1(s) + \frac{1}{2} \right] \tag{9}$$

Then

$$4\pi \int_{d_1}^{\infty} dz\, P(z) = \frac{-4\pi n z_0}{\kappa} \frac{\epsilon - 1}{\epsilon} \left[1 + \frac{\kappa \sigma}{2} \left(1 - \frac{1}{\lambda} \right) \right] \tag{10}$$

Substituting into eqn. (6) yields

$$\Delta V = -\frac{4\pi n}{\alpha^2} - 2\pi n z_0^2 + \frac{4\pi n z_0}{\kappa} \left\{ 1 + \kappa d_1 + \left(\frac{1 - \epsilon}{\epsilon} \right) \left[1 + \frac{\kappa \sigma}{2} \left(1 - \frac{1}{\lambda} \right) \right] \right\} \tag{11}$$

at the point of zero charge ($z_0 = 0$), this expression simplifies to

$$\Delta V = -4\pi n / \alpha^2 \tag{12}$$

The potential drop across the interface is a function of only n and α, which are metal parameters. This, however, does not mean that the potential ΔV is equal to the surface potential of the metal–vacuum interface χ_m, since α is also a function of the solution parameters. In the limit $\alpha \to \infty$ the electronic profile tends to $n(z) =$

$n\theta(z - z_0)$, and then eqn. (11) is not the same as the expression given in ref 14. There are two reasons for this discrepancy. First, the term $2\pi n z_0^2$ does not exist in ref. 14, because now the charge is not localized at the plane $z = 0$. Secondly, the third term in eqn. (11) is not that of ref. 14. However, if $d_1 = \sigma/2$ then they are identical. This means that an additional capacitance term appears because of the shift δ in the metal background profile.

The differential capacitance of the system is

$$\frac{1}{C} = \frac{\partial \Delta V}{\partial q_s} = -\frac{\partial \Delta V}{\partial q_M} = \frac{\partial \Delta V}{n \partial z_0} \tag{13}$$

using eqn. (11), we obtain

$$\frac{1}{C} = \frac{4\pi}{\kappa \epsilon}\left[1 + \frac{K\sigma}{2}\left(1 + \frac{\epsilon - 1}{\lambda}\right)\right] + 4\pi[\delta - z_0]$$

$$- 4\pi \frac{\partial}{\partial z_0}\left[1/\alpha^2\right] + 4\pi z_0 \frac{\partial d_1}{\partial z_0} \tag{14}$$

In this expression the first term of the right-hand side is the result of the MSA [7,8]. If the solvent molecules are shrunk to point dipoles ($\sigma_d \to 0$), one should recover, from eqn. (14), the differential capacitance of the MGC theory. Otherwise [14], one can define the effective dielectric constant

$$\bar{\epsilon} = \frac{\epsilon}{1 + \frac{\epsilon - 1}{\lambda}} \tag{15}$$

which then yields the MGC result with the effective dielectric constant $\bar{\epsilon}$. We must remark that in spite of the formal resemblance, the physics is different, since the solvent is polarized throughout the entire electric double layer.

The second term of eqn. (14) arises from the fact that the electrode charge is not localized at $z = 0$. The next term is due to changes in the dipolar surface layer of the metal as a function of the excess charge. And the last term reflects the fact that the distance d_1 is also a function of the excess charge. A detailed discussion of this fact can be found in ref. 3. At the point of zero charge this term vanishes.

Because of the intrinsic limitations of the MSA, we will limit ourselves to small surface charge densities around the point of zero charge. Thus, for a given value of d_1, we only need to compute α for the differential capacitance C.

(III) ELECTRONIC DENSITY PROFILE

The ansatz (3) on the electronic density profile is particularly convenient since $n(z)$ only depends on the parameter α. We will compute this parameter by minimizing the surface excess energy U_s. The kinetic energy and the non-coulombic part of the electron-neutralizing background are not affected by the presence of the solution, and therefore we use the expressions given in ref. 9 (eqn. 14 with $\alpha = \beta$).

$$U_{kin} + U_{exc} + U_{inh} \approx \frac{n}{\alpha}\left[-1.6423\, n^{2/3} + 0.25037\, n^{1/3} + 0.006584 \right]$$

$$+ \alpha n (\log 2)/72 \tag{16}$$

The pseudo-potential contribution U_{ps} to the energy is given by (eqn. 10 of ref. 1 with $\alpha = \beta$)

$$U_{ps} = \frac{2\pi n^2}{\alpha^3}\left[e^{-\alpha|z_0|} - \frac{e^{-\alpha R_M}}{2}\left(A_0 R_M + \frac{A_0}{\alpha} + 1 \right)(e^{\alpha z_0} + e^{-\alpha z_0}) \right.$$

$$\left. + \alpha\left(|z_0| + A_0 z_0^2/2 - A_0 R_M^2/2 - R_M \right)\right] + \frac{A_0}{\alpha} \tag{17}$$

where A_0 and R_M are the pseudo-potential parameters of Heine and Animalu (see also ref. 1).

The electrostatic energy is computed from the charge and polarization profiles, and the potential $V(z)$ which has been calculated in Appendix I. We find

$$U_{es} = \frac{\pi n^2}{2\alpha^3}\left[-8\alpha z_0 \theta(\alpha z_0) + 5 + 4\alpha z_0\, e^{-\alpha(d_1 - z_0)} \right.$$

$$\left. -4\, e^{-\alpha|z_0|} - \frac{2\alpha z_0\, e^{-\alpha(d_1 - z_0)}}{1 + \kappa/\alpha} \right]$$

$$- \frac{2\pi n}{\alpha}\int_{d_1}^{\infty} dz\, P(z)\, e^{-\alpha(z - z_0)} + C_t \tag{18}$$

The last term C_t consists of the remaining contributions to the energy which are not functions of α, and thus irrelevant to our calculation.

The penultimate term in eqn. (18) represents the interaction of the electrons with the local polarization of the solvent molecules in the solution. This contribution is easily calculated from the Laplace transform $\tilde{P}(s)$ (eqn. 7):

$$-\frac{2\pi n}{\alpha}\int_{d_1}^{\infty} dz\, P(z)\, e^{-\alpha(z - z_0)} = -\frac{2\pi n}{\alpha}e^{\alpha z_0}\tilde{P}(\alpha) \tag{19}$$

There is also another contribution due to the repulsive interactions of the electrons and the electronic clouds of the ions and solvent molecules [9]. These interactions are represented by Harrison's pseudo-potentials, with parameters λ_i (for ions) and λ_d (for solvent). This interaction is independent of the ionic charge or solvent dipolar orientation, and because of the use of the MSA, it will depend only on the total density profile $\rho_0(z)$. Since all the particles are hard spheres of equal diameter, a single parameter $\bar{\lambda}$ (a weighted average of λ_i and λ_d) will be enough for our purposes. We obtain

$$U_s = \bar{\lambda}\int dr \int dz'\, n(z)\delta(r - r')\rho_0(z') \tag{20}$$

$$\bar{\lambda} = \frac{\lambda_d \rho_d + 2\lambda_i \rho_+}{\rho_d + 2\rho_+}$$

$$U_{\text{kin}} + U_{\text{exc}} + U_{\text{inh}} = \frac{n}{\alpha}\left[-1.6423\, n^{2/3} + 0.25037\, n^{1/3} + 0.006584\right]$$

$$+\, \alpha n (\log 2)/72 \,. \tag{16}$$

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$$U_{\text{ps}} = \frac{2\pi n^2}{\alpha^3}\left[e^{-\alpha|z_0|} - \frac{e^{-\alpha R_M}}{2}\left(A_0 R_M + \frac{A_0}{\alpha} + 1\right)(e^{\alpha z_0} + e^{-\alpha z_0})\right.$$

$$\left. +\, \alpha\left(|z_0| + A_0 z_0^2/2 - A_0 R_M^2/2 - R_M\right)\right] + \frac{A_0}{\alpha} \tag{17}$$

where A_0 and R_M are the pseudo-potential parameters of Heine and Animalu (see also ref. 1).

The electrostatic energy is computed from the charge and polarization profiles, and the potential $V(z)$ which has been calculated in Appendix I. We find

$$U_{\text{es}} = \frac{\pi n^2}{2\alpha^3}\left[-8\alpha z_0 \theta(\alpha z_0) + 5 + 4\alpha z_0\, e^{-\alpha(d_1 - z_0)}\right.$$

$$\left. -\, 4\, e^{-\alpha|z_0|} - \frac{2\alpha z_0\, e^{-\alpha(d_1 - z_0)}}{1 + \kappa/\alpha}\right]$$

$$-\, \frac{2\pi n}{\alpha}\int_{d_1}^{\infty} dz P(z)\, e^{-\alpha(z - z_0)} + C_1 \tag{18}$$

The last term C_1 consists of the remaining contributions to the energy which are not functions of α, and thus irrelevant to our calculation.

The penultimate term in eqn. (18) represents the interaction of the electrons with the local polarization of the solvent molecules in the solution. This contribution is easily calculated from the Laplace transform $\tilde{P}(s)$ (eqn. 7):

$$-\frac{2\pi n}{\alpha}\int_{d_1}^{\infty} dz P(z)\, e^{-\alpha(z - z_0)} = -\frac{2\pi n}{\alpha}e^{\alpha z_0}\tilde{P}(\alpha) \tag{19}$$

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$$U_{\text{B}} = \bar{\lambda}\int dr \int dz\, n(z)\delta(r - r')\rho_0(z') \tag{20}$$

$$\bar{\lambda} = \frac{\lambda_d \rho_d + 2\lambda_i \rho_+}{\rho_d + 2\rho_+}$$

where ρ_d is the dipole concentration and ρ_+ is the $(+)$ ion concentration. The integration is easily performed:

$$U_B = \frac{\lambda n}{2} \int_{d_1}^{\infty} dz \, e^{-\alpha(z - z_0)} \rho_0(z) \tag{21}$$

$$= \frac{\lambda n}{2} e^{\alpha z_0} \tilde{\rho}_0(\alpha) \tag{21'}$$

where $\tilde{\rho}_0(\alpha)$ is the Laplace transform of the total density distribution function $(\rho_0(z) = \rho_d(z) + \rho_+(z) + \rho_-(z))$. We obtain

$$U_B = \rho_0 \frac{n\lambda}{2} e^{-\alpha(d_1 - z_0)} \frac{\beta_3^{(s)}}{(\beta_6^{(s)})^3} \frac{1}{\alpha \tilde{Q}(i\alpha)} \tag{22}$$

where $\beta_3^{(s)} = 1 + 2\eta$; $\quad \beta_6^{(s)} = 1 - \eta$; $\quad \beta_{12}^s = (1 + \eta/2)$ with

$$\eta = \frac{\pi}{6}(\rho_d + \rho_+ + \rho_-)\sigma^3$$

and

$$\tilde{Q}(i\alpha) = 1 - 12\phi_1(\alpha)\beta_{12}^{(s)}/(\beta_6^s)^2 - 12\eta\phi_2(\alpha)\beta_3^{(s)}/(\beta_6^s)^2$$

The functions $\phi_1(\alpha)$ and $\phi_2(\alpha)$ are defined by eqn. (9).

The total surface energy is then

$$U_s = U_{kin} + U_{exc} + U_{inh} + U_{ps} + U_{es} + U_B$$

Using eqns. (16)–(22) we obtain, finally,

$$\frac{U_s}{\pi n^2} = C_1/\alpha + C_2\alpha + \frac{1}{\alpha^3}\left[\frac{5}{2} - 2\alpha z_0 - \left[1 + \frac{A_0}{\alpha}(1 + \alpha R_M)\right] e^{-\alpha R_M}(e^{\alpha z_0} + e^{-\alpha z_0})\right.$$

$$- 2\alpha R_M + \frac{A_0}{\alpha}\left[2 + (\alpha z_0)^2 - (\alpha R_M)^2\right]\right]$$

$$+ e^{-\alpha(d_1 - z_0)}\left\{\frac{E}{\alpha \tilde{Q}(i\alpha)} + \frac{\alpha z_0}{\alpha^3}\left[2 + \frac{\alpha}{\alpha + \kappa}\left[-1\right.\right.\right.$$

$$\left.\left.\left.+ \frac{D}{A(\alpha)}\left[1 - \frac{\kappa\sigma}{1 + 1/\lambda}\left(\frac{1}{2\lambda^2} + \phi_1(\alpha)\right)\right]\right]\right]\right\} \tag{23}$$

The coefficients C_1, C_2, E and D, are given in Appendix 2.

In eqn. (23), all the electrostatic interaction terms with the solution cancel at $z_0 = 0$, the point of zero charge. The shift in the surface potential of the metal, when it is taken from the vacuum to the solution is due to the electron–solution repulsive interactions.

The minimization of U_s then yields α. This parameter is then used to compute the properties of the electrode with the aid of eqns. (11) and (19).

TABLE I

Values of the profile parameter α (Hg) as a function of d_1 and $\bar{\lambda}$. For the bare surface $\alpha_0 = 0.901$ a.u.

$\bar{\lambda}$	15	30	45
$d_1 = R_c + \sigma/2$	0.905	0.908	0.911
$d_1 = \sigma/2$	0.916	0.932	0.947

Two of the parameters of the problem are free, and have to be selected using physical intuition. They are δ and $\bar{\lambda}$. It seems realistic to choose the value of δ between 0 and R_c, the crystallographic radius of the ions in the metal [9].

For water the parameter $\bar{\lambda}$ has been estimated to be ~ 15. For DMSO we might expect an even higher value since there are 54 electrons in DMSO against 10 in water. In Table 1 we show the influence of $\bar{\lambda}$ on α assuming that $d_1 = \sigma/2$ or $d_1 = R_c + \sigma/2$. As expected, the repulsion term with the solution causes an increase in the values of α. This is similar to what we found previously [9]. In Fig. 3 we have plotted the shift in the surface potential of the metal $\delta\chi_m = 4\pi n(\frac{1}{\alpha^2} - \frac{1}{\alpha_0^2})$ calculated at the point of zero charge as a function of the distance d_1. The corresponding case of gallium for $\bar{\lambda} = 30$ is also shown.

The repulsion from the solution is not enough to keep the electrons in the region
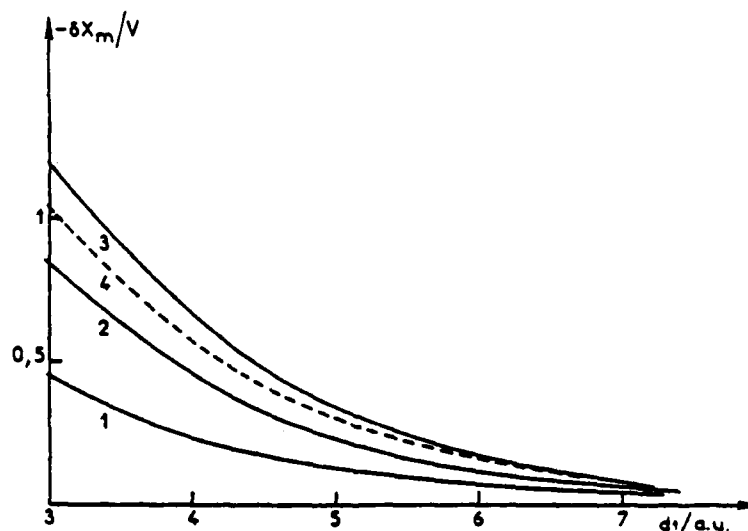

Fig. 3. Dependence of $\delta\chi_m$ on the parameter d_1 for different choices of $\bar{\lambda}$: (1) Hg $\bar{\lambda} = 15$; (2) Hg $\bar{\lambda} = 30$; (3) Hg $\bar{\lambda} = 45$; (4) Ga $\bar{\lambda} = 30$.
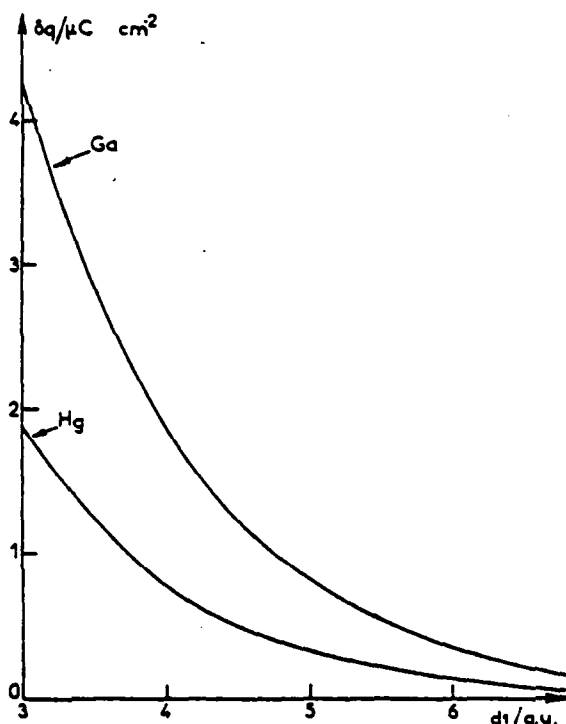
Fig. 4. Dependence of the charge spill-over δq on the parameter d_1 for Hg and Ga ($\bar{\lambda} = 30$ and $c = 0.1$ mol l^{-1}).

$z < d_1$. There is always a small charge spill-over, $-\delta q$, in the region $z > d_1$.

$$-\delta q = -\int_{d_1}^{\infty} dz \frac{n}{2} e^{-\alpha(z-z_0)} = -\frac{n}{2\alpha} e^{-\alpha(d_1-z_0)}$$

In Fig. 4 we show $\delta q(d_1)$ for both Hg and Ga. The spill-over δq is larger for Ga than for Hg.

In the simple model presented here, this effect has been neglected in calculating the charge distribution and the polarization in the solution. It is clear that this approximation is less justified for Ga than for Hg. However, the mathematical tools to include it are available and we will indeed discuss these effects in the near future.

The fact that there are electrons on the solution side even at the point of zero charge, indicates that the solvent molecules must be polarized at the interface even at the point of zero charge. Note that the ratio $\delta q(Ga)/\delta q(Hg)$ is not simply the ratio of the electronic densities.

The differential capacitances for the mercury electrode are given in Table 2. They were computed from the curve $\Delta V = f(q_M)$ by numerical differentiation. With the

TABLE 2

Differential capacitance of the interface $C/\mu F$ cm^{-2} as a function of d_1 and $\bar{\lambda}$. The concentration is $c = 0.1$ mol l^{-1}

$\bar{\lambda}$	d_1		
	$R_c + \dfrac{\sigma}{2}$	$\dfrac{\sigma}{2} + 0.1$ nm	$\dfrac{\sigma}{2}$
15	9	20.8	100
30	9	18.7	58.8
45	8.7	16.6	43.4

parameters of this article the zero charge capacitance corresponding to an ideal metal would be

$$C_1 = \frac{\kappa}{4\pi} \frac{\epsilon}{1 + \frac{\kappa\sigma}{2}\left(1 + \frac{\epsilon - 1}{\lambda}\right)} = 7.94 \ \mu F \ cm^{-2}$$

We see that the total capacitance depends crucially on the distance d_1.

When d_1 is large the value of C is greater than C_1 but the effect of non-ideality of the metal remains small. On the other hand, when the distance of closest approach decreases (for instance if there is interpenetration between the metallic ions and the particles of the solution) this effect becomes quite important and the influence of $\bar{\lambda}$ is not negligible (for comparison the experiment value of 18 μF cm^{-2} for $LiClO_4$ ions [15]).

First calculations show that the differential capacitance for Ga would be greater than for Hg, as observed experimentally.

(V) CONCLUSIONS

We have presented a realistic model of the metal–solution interface, in which the metal is not an ideal smooth metal, but a jellium model. A simple discussion of this model is given. The results confirm earlier calculations [1–4] that indicate that the metal makes an important contribution to the differential capacitance C.

The solution side of our model is a mixture of hard spheres with charges and point dipoles. No a priori separation of compact and diffuse layers is postulated in this model, and it also does not involve the use of local dielectric constants (a meaningless quantity). The calculations show that the solvent molecules are polarized even at the point of zero charge. This is so because of the spill-over of electronic charge into the solution, which produces non-zero electric fields in the metal–solution boundary layer. Although we have treated this effect only crudely, the recent work on the GMSA [16] of the ion–dipole mixture allows a consistent calculation of this effect.

We also show that the distance d_1 of closest approach of the metal ions and the solution ions is a crucial parameter in the determination of the differential capacitance C. However, this is also a drawback since the fact that d_1 is unknown makes

266

the comparison of C with experiment a not very meaningful exercise. Indeed a value of d_1 which fits the experiments could be found.

However, the model that we have discussed here represents the most comprehensive one that we are aware of. We are undertaking a detailed study of the influence of various parameters, such as ionic concentration, density and dipole moment of the solvent, etc. on the differential capacitance. The results will be published in the near future.

APPENDIX 1

Electrostatic potential profile

Integrating eqn. (5), obtain (also using eqns. 1 and 3)
(a) For negative metal charge q_M ($z_0 > 0$):

$$V(z) = -\frac{2\pi n}{\alpha^2} e^{\alpha(z-z_0)} \qquad (-\infty < z < 0)$$

$$V(z) = 2\pi n(z^2 - e^{+\alpha(z-z_0)}/\alpha^2) \qquad (0 < z < z_0)$$

$$V(z) = 2\pi n\left[z_0(2z - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2\right] \qquad (z_0 < z < d_1)$$

$$V(z) = 2\pi n\left[z_0(2d_1 - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2\right] + 4\pi n z_0/\kappa$$

$$\qquad + 4\pi \int_{d_1}^{z} dz' P(z') - \frac{4\pi n z_0}{\kappa} e^{-\kappa(z-d_1)} \qquad (z > d_1)$$

(b) For positive q_M ($z_0 < 0$):

$$V(z) = -\frac{2\pi n}{\alpha^2} e^{\alpha(z-z_0)} \qquad (-\infty < z < z_0)$$

$$V(z) = -2\pi n\left[(z-z_0)^2 + 2/\alpha^2 - e^{-\alpha(z-z_0)}/\alpha^2\right] \qquad (z_0 < z < 0)$$

$$V(z) = 2\pi n\left[z_0(2z - z_0) - 2/\alpha^2 + e^{-\alpha(z-z_0)}/\alpha^2\right] \qquad (0 < z < d_1)$$

For $d_1 < z < \infty$ the equations are those of the case $q_M < 0$.

APPENDIX 2

We give explicit formulae for the coefficients of eqn. (23):

$$C_1 = \frac{1}{\pi n}\left[-1.6423 n^{2/3} + 0.25037 n^{1/3} + 0.006584\right]$$

$$C_2 = \frac{1}{\pi n}\frac{\log 2}{72}$$

$$E = \frac{\lambda}{2\pi n}\rho_0\frac{(1+2n)}{(1-\eta)^2}$$

$$D = \frac{8\pi\mu^2\rho_d}{kT\lambda(2+\lambda)}$$

These coefficients are computed once and for all for a given metal and solvent.

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-8